ELECTRON SPIN RESONANCE STUDIES OF TRANSIENT RADICAL-IONS IN LIQUID AMMONIA

by

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ABSTRACT

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This work describes the use of electron spin resonance spectroscopy in investigations of the reduction of a number of organic compounds by solutions of sodium in liquid ammonia. Solutions of alkali metals in ammonia contain the ammoniated electron, in all its possible forms, and essentially this species is the effective reducing agent. The simple reduction step is the one-electron addition to a suitable substrate molecule, which may then undergo a number of successive reactions before a stable product is formed. The nature of the metal-ammonia solutions, and the paths the reductions may take are discussed in Chapter 2.

The simple one-electron reduction product, a radical-anion, is often too short-lived to allow observation by normal static methods, and therefore a relatively high concentration of radicals must be artificially maintained to permit their detection. Basically two different approaches have been utilised :

(i) stabilising the radicals either by direct production or trapping in a solid matrix, therefore preventing the radicals from reacting, and

(ii) production of a high steady state concentration of radicals in solution by either continuous electrolysis or by use of a flow system.

A brief discussion of the methods used in the study of transient radicals is given in Chapter 1. Generally the e.s.r. spectra are less well-resolved in solid matrices than in solution, and for species showing a large amount of hyperfine structure, production of the radicals in solution is preferred.

A rapid mixing device has been developed to allow observation of transient intermediates by e.s.r. spectroscopy. The mixer was designed particularly for the type of system and experimental technique under consideration here, and is based on a design used in biological kinetic studies.

Observations 2 - 5 msec. after mixing are possible, and this represents a considerable advantage over the more widely used aqueous solution mixing device, where observations are made on a 10^{-2} sec. time scale. The mixing chamber and experimental technique are presented in Chapter 3.

Analysis of the e.s.r. spectrum of a compound allows the calculation of its unpaired electron distribution, the coupling constants being related to the unpaired electron spin density. Spin densities have been calculated theoretically, and it has been found that simple Hückel calculations of pi-electron spin densities show good agreement with "experimentally" determined values. Accordingly, both Hückel and McLachlan spin densities have been calculated for most of the substrates used, and in general it is found that the McLachlan treatment gives better agreement with experiment than the simple Hückel model. A brief discussion of the relevant molecular orbital theory is presented in Chapter 1, and the computer programme used to perform the theoretical calculations is given in Appendix 3. Analysis of the e.s.r. spectra is sometimes very difficult if a large number of lines are present, and two computer programmes used for the simulation of single and mixed e.s.r. spectra are given in Appendices 2 and 3, respectively.

In Chapter 4 is described the reduction of a number of aryl halides. With the exception of fluoro-substituted compounds, the halo-pyridines, pyrimidines, benzenes, biphenyls, and naphthalene all give the e.s.r. spectrum of the radical-anions of the parent compounds on reduction. On the other hand, fluorine is retained as is evident from the spectra, for a much longer period, as shown by observations 0.1 and 1.0 sec. after mixing, while static experiments show some products to be stable for longer periods of time in this system. Mechanisms have been proposed to account for these reductions. Halobenzonitriles have also been studied and the results are in agreement with the proposed reduction mechanisms.

Reduction of pyridine, pyrimidine and some simple ring-substituted

compounds has been investigated, and their e.s.r. spectra characterised in most cases. Previous attempts to observe the pyridine radical-anion had failed, the spectrum of the 4,4'-bipyridyl being obtained instead. Observations 0.1, 1.0 sec. and 1 min. after mixing allow the reduction path of these nitrogen heterocyclics to be followed, and it is shown that pyridine, pyrimidine and simple alkyl- and alkoxy-substituted pyridines undergo dimerisation to give exclusively the respective 4,4'-dimers, unless the 4-position is blocked. Pyridine-N-oxide undergoes a more complex reduction, giving pyridine-N-oxide, pyridine and finally 2,2'-bipyridyl radical-anions. Pyridine-3- and 4-carboxylic acids give spectra of the radical-anions, while pyridine-2-carboxylic acid gives a spectrum suggesting some form of nitrogen-hydrogen bonded species. Pyridine dicarboxylic acids all have one feature in common, a splitting from an extra proton which arises through a protonated nitrogen atom. Reduction of pyridine in the presence of excess ethanol also shows this feature, and its spectrum is due to $C_5H_5NH\cdot$.

Calculation of the nitrogen sigma-pi interaction parameters gives values of $Q_N^N = +28.5$ oe. and $Q_{CN}^N = -0.5$ oe., in good agreement with results obtained previously. Theoretical calculations have been performed, and comparison with experiment has enabled the assignment of coupling constants to particular positions, and also gives the best set of parameter values required for the calculations, providing a check with values used for comparison with other measurements. The results are presented in Chapter 5.

In Chapter 6 is described the reduction of benzoic acid and some of its simple ring-substituted derivatives. Ionisation occurs initially, followed by reduction to give the corresponding radical-anions. These species are short-lived, as no spectra are obtained when observations are performed 0.1 sec. after mixing. No further paramagnetic products are found. Molecular orbital calculations have been performed for each compound, and excellent agreement with experiment obtained using the parameter values

$k_{C'-C} = 1.2$, $k_{C-O} = 1.6$, $h_O = 2.0$ for the ionised carboxy group.

Reduction of nitro-substituted isophthalic and terephthalic acids shows the presence of two distinct species, one being unstable while the other is stable for more than one hour, in both cases. The unstable species show a large splitting from an extra proton which is thought to be attached to the nitrogen atom. This proton is lost to give the stable radicals, experimental evidence and comparison with computer calculations suggesting them to be the nitro-substituted radical-anions.

CHAPTER 1

GENERAL INTRODUCTION

1.1. INTRODUCTION

Chapter 1 is essentially an introductory chapter, dealing briefly with the principles of electron spin resonance spectroscopy, the relationships between the experimental coupling constants and unpaired pi-electron spin densities, and methods which have been used to generate and observe transient radicals.

The basic principles involved in an electron spin resonance experiment are given, and the expressions for the experimentally observable coupling constants derived. These coupling constants are proportional to the unpaired spin densities in pi-electron radicals, and a knowledge of such an electronic distribution is useful in explaining the properties and reactions of these radicals. Assignment of the coupling constants to particular ring positions is essential before such an electronic distribution can be obtained, and this is sometimes difficult where the molecule in question is magnetically unsymmetrical. This problem can be solved by comparison of the "experimental" spin densities with theoretically calculated spin densities, which permits such an assignment to be made. Spin densities have been calculated by two methods, and the details of these treatments are presented in Section 1.3.

One-electron reduction leads to products which are often too short-lived to be observed by the usual static methods, and therefore some means of maintaining a sufficiently high concentration of radicals for detection and observation is required. This has been achieved in liquid solution by continuous electrolysis or by the use of a flow system, and in the solid state by direct production or trapping in a solid matrix of either the material under consideration or an inert material. A large number of compounds have been studied by utilising these techniques and brief details are given in Section 1.4.

1.2. ELECTRON SPIN RESONANCE

1.2.1. Basic Principles

Electron spin resonance (e.s.r.) spectroscopy, as its name implies, depends upon the property of spin associated with an unpaired electron. This gives rise to a magnetic moment

$$\vec{\mu}_e = -g\beta\vec{S}$$

where g is the electronic spectroscopic splitting factor, β is the electronic Bohr magneton and $\vec{S}\hbar$ is the spin angular momentum vector of the electron.

In the presence of an externally applied magnetic field $\vec{H}$, interaction between the electron magnetic moment and the field occurs. This interaction is represented by the Hamiltonian

$$\mathcal{H} = -\vec{\mu}_e . \vec{H} = g\beta\vec{S} . \vec{H}$$

If the applied magnetic field is in the z-direction, the Hamiltonian becomes

$$\mathcal{H} = g\beta S_z H$$

where S_z is the component of the electron spin in the z-direction and H is the field strength in the z-direction. For a single electron with spin $S = \frac{1}{2}$ there are $2S + 1 = 2$ allowed orientations for the spin, either parallel or antiparallel to the field H, and these are characterised by the quantum numbers $M_s = +\frac{1}{2}$ and $M_s = -\frac{1}{2}$ respectively.

Similarly, interaction of a nucleus of spin I with the steady magnetic field gives an energy

$$\mathcal{H} = -g_N\beta_N I_z H$$

where g_N is the nuclear g-factor, β_N is the nuclear magneton and I_z the component of the nuclear spin in the z-direction. The Hamiltonian representing the interaction of both an electron and a nucleus with a steady magnetic field,

the so-called Zeeman interaction, is therefore

$$\mathcal{H}_z = g\beta S_z H - g_N \beta_N I_z H \qquad (1)$$

Coupling between the magnetic moment vectors of the electron and nuclei may occur in two distinct ways. One is isotropic and is the Fermi contact interaction, which is given by

$$\mathcal{H}_c = a\vec{I}.\vec{S} = \frac{8\pi}{3} g\beta g_N \beta_N \delta(\vec{r}).\vec{I}.\vec{S}$$

The δ-function implies that there must be electron spin density at the nucleus for contact interaction to occur. The coupling constant a is proportional to the electron spin density at the nucleus.

The second form of interaction is anisotropic and is analogous to the classical interaction between two dipoles. The Hamiltonian for this dipolar interaction is

$$\mathcal{H}_d = -g\beta g_N \beta_N \left(\frac{\vec{I}.\vec{S}}{r^3} - \frac{3(\vec{I}.\vec{r})(\vec{S}.\vec{r})}{r^5} \right)$$

where r is the distance between the electron and nucleus. The dipolar interaction averages to zero for a molecule with spherical symmetry.

Accordingly, the complete Hamiltonian for a molecule with spherical symmetry is given by

$$\mathcal{H} = g\beta S_z H - g_N \beta_N I_z H + a S_z I_z \qquad (2)$$

and in the high-field limit this "spin" Hamiltonian gives rise to the energy levels

$$E = (g\beta M_s - g_N \beta_N M_I)H + a M_s M_I \qquad (3)$$

where M_s and M_I are the spin quantum numbers for the electron and nucleus respectively and a is the hyperfine coupling constant for the nucleus.

For a single unpaired electron two levels exist with energies $+\frac{1}{2} g\beta H$ and $-\frac{1}{2} g\beta H$ and transitions between these two levels will occur if radiation

of energy $h\nu$ (where ν is the frequency), equal to the difference in energy between the two states, is applied. These transitions are governed by the selection rules $\Delta M_s = \pm 1$ and $\Delta M_I = 0$. The relative populations of the two levels are governed by a thermal distribution and transitions from the lower to the upper state will predominate with a net absorption of the incident radiation. The resonance condition will therefore be

$$h\nu = g\beta H \tag{4}$$

For the case of an electron interacting with a single nucleus, the resonance condition becomes

$$h\nu = g\beta H + aM_I$$

Weissman[1] has shown that for molecules tumbling rapidly in solution, the dipolar part of the interaction averages to zero. This gives the molecule an average spherical symmetry and thus to a good approximation the e.s.r. spectra of most radicals in solution can be described by equations such as (2) and (3) above.

1.2.2. Hyperfine Splitting and Spin Density in PI Conjugated Organic Radicals

For hyperfine interaction to occur there must be some unpaired electron density at the nucleus in question, i.e., the unpaired electron must have a certain amount of s-orbital character. In the radicals described in this work, the unpaired electron is in a pi-orbital which has a node in the molecular plane. In the approximation of independent sigma- and pi-electrons in organic molecules, it is difficult to see how the wealth of hyperfine structure exhibited by radicals derived from such molecules arises, as the contact term is expected to be zero for nuclei in the nodal plane. Once it had been determined[2-6] that the hyperfine structure of some aromatic molecules was due to nuclei attached to the ring carbon atoms, it became necessary to account for spin density at the nuclei. Zero-point vibrations of the protons[2] and an indirect

coupling between the electron and proton magnetic moments through the chemical bond[5] were proposed initially. Out of plane vibrations of the protons were ruled out by the lack of dependence of the coupling constants of the hydrogen isotopes on their atomic weights.[7] Polarisation of the sigma electrons by sigma-pi configurational interaction has been used by several authors[8-11] and this approach appears to give the best results. Proton hyperfine interaction has been studied extensively due to its importance in the analysis of free radical spectra. McConnell[8] proposed that the proton coupling constant a_{CH}^{H} is directly proportional to the unpaired electron density ρ_c in the pi atomic orbital of the carbon atom to which the proton is bonded

$$a_{CH}^{H} = Q_{CH}^{H} \rho_c \qquad (5)$$

where Q_{CH}^{H} is the sigma-pi interaction parameter. Further theoretical work[12-15] has confirmed this, as have a vast number of experimental studies reported in the literature. However, despite the success of the theory, the value of Q_{CH}^{H} varies depending upon the bonding of the trigonal carbon atom. A value of -23.7 Oe, based on theoretical considerations and a comparison of the ^{13}C splitting observed in the methyl radical has frequently been used.[16]

McLachlan[17] has carried out a valence bond treatment to account for the splitting exhibited by methyl group protons, arriving at a result similar to that for proton splitting

$$a_{CH_3}^{H} = Q_{CCH_3}^{H} \rho_c \qquad (6)$$

$a_{CH_3}^{H}$ is the methyl proton coupling constant and ρ_c is the electron spin density on the trigonal carbon atom. $Q_{CCH_3}^{H}$ is the spin polarisation parameter and is given a value of 28 Oe. Levy[18] calculated methyl and methylene hyperfine coupling constants based on a hyper-conjugative model for the substituents.

Applying configuration interaction techniques similar to those in the earlier work, Karplus and Fraenkel[16] derived an expression for the hyperfine coupling a^C of an sp^2-hybridized ^{13}C atom

$$a^C = (S^C + \sum_i^3 Q_{CX_i}^C)\rho + \sum_i^3 Q_{X_iC}^C \rho_i \qquad (7)$$

where ρ and ρ_i ($i = 1, 2, 3$) are the pi-electron spin densities on atoms C and X_i, respectively. The contribution of the 1s-electrons to polarisation of the bonds is determined by S^C and that of the 2s-electrons by the Q's, where Q_{CX}^A is the sigma-pi parameter for the nucleus of atom A resulting from the interaction between the bond C - X and the pi-electron spin density on atom C. The constants in the equation were evaluated.

The Karplus-Fraenkel method is applicable to all appropriately bonded elements in the first row of the periodic table. In particular, it has been used extensively to interpret nitrogen hyperfine coupling, when the equation becomes[19]

$$a^N = Q_N^N \rho_N + \sum_i Q_{X_iN}^N \rho_i \qquad (8)$$

a^N is the nitrogen coupling constant, ρ_N and ρ_i the pi-spin densities on the nitrogen atom and the other atoms bonded to the nitrogen, respectively. Q_N^N has been written for $(P^N + \sum_i Q_{NX_i}^N)$. P^N and $Q_{NX_i}^N$ represent the polarisations of the nitrogen 1s- and 2s-electrons, respectively. $Q_{X_iN}^N$ is a sigma-pi parameter representing polarisation of the N - X_i bond by spin density on the X_i atom.

1.2.3. Analysis of Spectra

Generalisations about the analysis of e.s.r. spectra are impossible. In some cases, when the radical has few interacting nuclei, the pattern of spectral lines is obvious by inspection. For more complex systems a knowledge of the splitting patterns for all equivalent groups of nuclei in

the molecule will be of assistance in analysis. In particular, care must be taken to ensure that low intensity lines in the extreme wings of the spectrum are not accidentally missed. In doubtful cases the spectrum should be over-modulated in order that the wing lines become discernible. Less overlap of lines occurs in the wings of the spectrum, hence related groups of lines are more obvious and partial analysis can result from careful inspection of the spectrum in this region. Theoretical spectra obtained by considering likely combinations of the coupling constants can then be constructed, either in the form of a "stick-plot" or with the aid of a computer. In this work spectra have been simulated by computer. This method has the great advantage of giving accurate intensities of non-overlapping and overlapping lines as well as line positions. Suitable alteration of the coupling constants and linewidth can then be made in order to obtain an accurate fit of simulated spectrum with experimental spectrum. Good agreement between simulated and experimental spectrum is taken as indicative of correct analysis.

Two programmes have been used for this purpose. One involves the input of more data and was used for molecules containing a large number of equivalent nuclei. The outputs for both programmes are identical. The main programme is given in Appendix 1.

Careful examination of some spectra indicate the presence of two paramagnetic species. When such cases occur, analysis is relatively easy if one species is in excess, but if the amounts of each radical are comparable, analysis presents a much greater problem. Only accurate measurements of line positions and intensities reveal the details of each component spectrum, and if a tentative analysis for each can be made, simulated spectra can be obtained and superimposed. This procedure is very unsatisfactory as overlap of lines is ignored, and a programme has been written to simulate such spectra, allowance being made for different intensities and line widths, permitting more accurate interpretation. The programme is given in Appendix 2.

Once a set of hyperfine coupling constants is determined which will reproduce exactly the experimental spectrum, it then remains to assign the coupling constants to particular positions in the molecule. In some cases this is facile, for example when all positions are equivalent, as in the benzene radical-anion, or where all magnetically equivalent positions give different splitting patterns, as in the radical-anion of 3,5-dimethyl pyridine. Assignment of the coupling constants in ambiguous cases is more open to doubt but may be achieved in various ways. Substitution at certain positions by deuterium changes the coupling constant and splitting pattern for those positions, while leaving the rest of the molecule approximately unperturbed. Coupling constants may then be assigned to particular positions. Methyl substitution can also be used, although this causes greater perturbation of the system.

Alternatively, comparison of theoretically calculated spin densities with experimentally determined ones may lead to assignation of the corresponding coupling constants. "Experimental" spin densities are obtained from the hyperfine coupling constants by application of equations (5) to (8) above. Calculations of theoretical spin densities are discussed in the following section.

1.3. THEORETICAL STUDIES OF PI-CONJUGATED ORGANIC RADICALS

Theoretical spin densities have been calculated for all the systems considered to obtain a correlation between simple molecular orbital (MO) theory and the experimentally determined hyperfine coupling constants. Calculations were carried out using the simple Hückel linear combination of atomic orbitals (LCAO) method,[20] and the approximate configuration interaction treatment of McLachlan.[21]

In the Hückel molecular orbital (HMO) method, the sigma- and

pi-bonds are treated as non-interacting, the sigma-orbitals being localised into bonds, whereas the pi-orbitals are formed as a linear combination of the $2p_z$-atomic orbitals of the conjugated atoms. These atoms are assumed to share the same nodal plane. Each LCAO MO can therefore be written in the form

$$\Psi_j = \sum_i^n C_{ij} \phi_i$$

where Ψ_j is the jth MO, ϕ_i is the atomic orbital of the ith atom ($2p_z$ orbitals for our purposes) and C_{ij} is the coefficient of the ith atomic orbital in the jth MO. These MO's are eigenfunctions of a Hamiltonian operator (considered for the pi-system alone), which on solution, gives the set of coefficients for the best energy value of the molecular orbital. Solution is effected by applying the variation principle, and reduces to the solution of a set of simultaneous homogenous linear equations, the secular equations, of the form

$$\sum_r C_r(H_{rs} - E.S_{rs}) = 0$$

where $H_{rs} = \int \phi_r \mathcal{H} \phi_s \, d\tau$ and $S_{rs} = \int \phi_r \phi_s \, d\tau$. The terms H_{rr}, the diagonal matrix elements are the Coulomb integrals and H_{rs} for $r \neq s$, the off-diagonal matrix elements are the resonance or bond integrals. In the Hückel method the interaction energy between non-bonded atoms is taken as zero, hence H_{rs} for r not bonded to s is zero. The integrals S_{rs} are the overlap integrals. The assumption is made that $S_{rs} = 1$ for $r = s$ and $S_{rs} = 0$ for $r \neq s$. E in the above equation is the energy of the molecular orbital r. Solution of the secular equations yields n values for the energy given as an algebraic sum of a Coulomb integral and some multiple of a resonance integral

$$E = \alpha + m_j \beta$$

α is the Coulomb integral for an sp^2-bonded carbon atom and β is the resonance integral for a carbon-carbon bond in benzene. Although both α and β are negative energy quantities, the convention is to take α as the relative energy zero, then the energy levels can be represented by levels above ($m_j < 0$) and below ($m_j > 0$) this zero. For positive m_j the orbitals are termed bonding MO's, while for negative m_j they are termed anti-bonding MO's. In certain cases m_j can be zero when the energy of the MO is the same as that of any constituent carbon 2p-orbital. This is termed a non-bonding MO. Once the values of the energy of each MO have been found, the values of the coefficients may be determined and hence the eigenvalues (energies) and eigenvectors (coefficients) of each MO can be obtained.

In the systems under consideration here, all are alternant and so each bonding MO is filled with two paired electrons in the neutral molecule. In the radical-anion, the extra electron is accommodated in the lowest-energy antibonding MO, which therefore determines the properties of the radical-anion, enabling the determination of the spin density at each atom in the molecule. The unpaired electron density at atom i in the jth MO can be shown to be C_{ij}^2. In HMO theory this is equivalent to the spin density ρ_i at that atom. Therefore, the spin density distribution in a radical-anion is given simply by the squares of the coefficients at each atom position in the lowest-lying antibonding MO.

Good agreement between spin densities obtained from HMO theory and those determined experimentally has been found for even alternant hydrocarbons such as naphthalene[22,23] and perylene.[23-25] In the case of radicals derived from odd alternant hydrocarbons such as triphenylmethyl[26,27] and perinaphthenyl[28] agreement between experiment and theory is rather poor. HMO theory predicts the existence of zero spin density for certain positions, while finite couplings are apparent in the e.s.r. spectra. To explain these and similar observations in other species it has been pointed

out that hyperfine interaction can be either positive or negative, thus the corresponding spin densities can be of either sign. The simple HMO theory must therefore be modified in order to account for this effect, as inherently it can predict no negative spin density, and this is achieved by considering the interactions of electrons with one another.

It has been done in a particularly useful way for comparison with e.s.r. measurements by McLachlan.[21] The method is based on SCF theory but it may be formulated in HMO parameters as

$$\rho_r = C_{ro}^2 - \lambda \sum_s \pi_{rs} C_{so}^2 \qquad (9)$$

In this equation ρ_r is the spin density at atom r in the MO containing the odd electron. C_{ro} is the Hückel coefficient of the rth atom of the odd orbital, π_{rs} is the atom-atom polarisability of atoms r and s defined by

$$\pi_{rs} = -4 \sum_i \sum_j \frac{C_{ri} C_{sj} C_{si} C_{rj}}{E_j - E_i}$$

where i and j are the occupied and vacant orbitals, respectively, and E_i are the Hückel energy level values. λ is an adjustable parameter derived from the theory, the most general value of which is taken as 1.2 β-units. The summation in equation (9) is taken over all atoms s. The largest part of the spin density is due to the electron in the lowest antibonding orbital, while the unpaired spins of the half-filled electron shell give a small correction. These corrections can lead to negative spin densities.

Application of the McLachlan technique gives in most cases, better agreement with experiment than the HMO method. It is in better agreement with the total width of e.s.r. spectra which are generally wider than the 23.7 Oe value expected if negative spin densities were absent. All positions which the HMO treatment predicts to be zero have negative spin densities,

while numerically larger values occur for the other positions. This must be so in order that $\sum_i \rho_i = 1$ which must hold in a conjugated radical.

Although both α and β were defined in terms of core Hamiltonians, they can be modified to include the average effects of other electrons, hence α is expected to vary from carbon to carbon and β will vary with bond length. These variations will be particularly felt if heteroatoms are present in the conjugated system. Such changes due to heteroatoms can be incorporated in the theory by appropriate changes in the empirical α and β parameters, by the definitions

$$\begin{aligned} \alpha_X &= \alpha_o + h_X \beta_o \\ \beta_{C-X} &= k_{C-X} \beta_o \end{aligned} \qquad (10)$$

α_X and β_{C-X} are the Coulomb and resonance integrals, respectively, associated with the heteroatom X. α_o and β_o are the corresponding integrals in sp^2-bonded carbon pi-systems.

The theoretical calculations were carried out on an I.C.L. (Elliott) 4130 computer, as were the spectra simulations. The programme for the spin densities consists basically of the matrix solution of the secular equations, giving the eigenvalues and eigenvectors. Procedures have been written to minimise the input data and to calculate and output Hückel and McLachlan spin densities for radical-anions. The programme and its mode of operation are given in Appendix 3.

Comparative theoretical studies are useful in ways other than for assignment purposes. E.s.r. provides a sensitive method for obtaining spin distributions in molecules, hence variation of the empirical parameters involved in the MO calculations can be carried out to obtain the best fit with experiment. Through the MO calculations comparison may be made with the e.s.r. data and polarographic or spectrophotometric data of a molecule. Details of the stereochemistry of a molecule can, in some

cases, be determined by e.s.r. and this can be followed by manipulation of the theoretical data.

1.4. METHODS OF STUDY OF TRANSIENT RADICALS

Many radicals are, of course, sufficiently stable to be examined by e.s.r. at leisure either at ambient temperatures or simply on cooling the sample to, say, -80°C. More rapidly decaying radicals can be stabilised by preventing diffusion through working at very low temperatures. Alternatively, a sufficiently high steady-state concentration of radicals can be maintained to overcome the rapid decay.

Both possibilities have been realised in many instances and exhaustive coverage is available in review articles.[29] Particularly important examples of these general techniques are radiolysis, photolysis, electrolysis and the use of flow systems, and these are now covered.

1.4.1. Radiolysis

Radicals have been identified following radiolysis both of gases (by trapping from a stream of gas on to a cold finger) and of solids (by in situ irradiation). Unless one is dealing with single crystals, the e.s.r spectra are marred by line-broadening. Nonetheless, radiation-induced e.s.r. spectra of both glassy and polycrystalline solids and solutions have given information both on the electronic structure of the radicals and on the radiolytic process.

Alkyl radicals have been obtained on γ-irradiation at 77°K of alkyl halides[30,31] and aliphatic hydrocarbons,[32] the latter also giving alkyl radicals on continuous irradiation with 2.8 MeV electrons in the liquid state.[33] X- or γ-irradiation of aliphatic alcohols, aldehydes and ketones[32,34] produces radicals by selective alpha-hydrogen abstraction. Carboxylic acids,[35] amides,[36] and particularly amino acids[37] have been irradiated and their

e.s.r. spectra determined, both in single crystals and polycrystalline states. Radiolysis and e.s.r. examination[38] of frozen neutral acid and alkaline aqueous solutions has provided details of the primary radiolytic species, including the trapped electron. E.s.r. has been used for the characterisation of radicals formed during irradiation of polymers.[39]

1.4.2. Photolysis

Photolysis with u.v. or visible light in both solid and liquid phases gives rise to radicals, the latter exhibiting better resolved e.s.r. spectra. Observations of short-lived radicals in liquid solution is effected by flowing the solution through the cavity during intense irradiation.

Transparency of the matrix is an essential requirement for photolyses in solid matrices, and is met by the inert gases. Small alkyl radicals[40] and small inorganic radicals[41] have been prepared in such systems. When frozen, alcohols[42] are transparent, and give well resolved e.s.r. spectra on photolysis. Similar e.s.r. spectra are obtained when simple alcohols containing about 1% hydrogen peroxide undergo intense u.v. irradiation.[43] Oxidation of aliphatic compounds by high valence metal ions can be initiated by photolysis at low temperatures.[44]

1.4.3. Rotating Cryostat

One-electron transfer from a donor such as sodium to an acceptor such as a halohydrocarbon forms the basis of the method. The two reactants are mixed intimately by directing them in gaseous streams on to the outer surface of a rapidly rotating drum (ca. 2400 r.p.m.) filled with liquid nitrogen, under high vacuum.[45] Chemical reaction occurs and the deposit, containing radicals or radical-anions derived from the acceptor, is transferred to an e.s.r. sample tube. Radicals are formed by the reaction

$$RX + Na\cdot \rightarrow R\cdot + NaX$$

Radicals such as $CO_2^{\mp}$,[46] $CS_2^{\mp}$,[47] alkyls,[45] phenyl,[48] aliphatic ketyls[49] and trapped electrons[50] have been obtained. Generally the spectra tend to be ill-resolved compared to solution spectra because of dipolar broadening.

1.4.4. Flow Systems

Flow systems incorporating the mixing device described by Dixon and Norman[51] have been widely exploited for solution studies of short-lived radicals. Studies of aqueous solutions necessitate the use of the flattened aqueous cell, and the flow system is based on this, the reactants being mixed just outside the resonant cavity and then flowed into the flat portion. Examples of the systems investigated by this technique are discussed briefly below.

Reaction of the titanous ion-hydrogen peroxide system with many simple organic compounds results in the formation of radicals by cleavage of carbon-hydrogen bonds, e.g., the radical $\cdot CH_2OH$ from methanol solutions.[51] The relative activating or deactivating effect of substituent groups can be inferred from this type of measurement[52] and electron transfer reactions in solution, e.g., from $\cdot CH_2OH$[51] or $CO_2^{\mp}$[53,54] to electron acceptors have been observed. Oxidations using acidic ceric solutions give the short-lived aryloxy,[55] meta-semiquinone[56] and anilino radicals.[57] Nitrobenzene and substituted nitrobenzene radical-anions have been obtained by reduction of the parent compound using basic sodium dithionite solutions.[58]

Further applications of flow systems include the incorporation of plugs of lead dioxide or silver oxide to achieve heterogenous oxidation.[59]

1.4.5. Electrolytic Reduction

In situ electrolysis sometimes enables a sufficiently high steady-state concentration of radicals to be maintained for e.s.r. measurements to be made. Radical-anions are formed by one-electron reduction at the cathode which is placed in the centre of the resonant cavity. Reduction products of parent molecules such as nitro-compounds,[60] nitriles,[61]

ketones[62,63] (some of which exhibit restricted rotation) are observed. The radical-anions of butadiene,[64] nitrosobenzene[65] and some nitrogen-containing heteroaromatics such as pyridine, pyrimidine and some of their ring-substituted derivatives[66] have been generated electrolytically in liquid ammonia.

CHAPTER 2

AMMONIA SYSTEMS

2.1. METAL-AMMONIA SOLUTIONS

It has been known for many years that solutions of alkali or alkaline earth metals in liquid ammonia possess very powerful reducing properties, although their nature is by no means well understood. In the first quantitative studies on these solutions, Kraus[67] deduced from conductance measurements that the positive electrolytic carrier is the metal cation and the negative carrier is the solvated electron. It was found that the electron carries about seven-eighths of the total charge. To account for this behaviour, Kraus proposed that the alkali metals, M, exist in equilibrium with solvated metallic cations, M^+, and ammoniated electrons, e^-_{amm}

$$M = M^+ + e^-_{amm}$$

However, Husters[68] observed decrease in the molar paramagnetic susceptibility with increasing metal concentration necessitated further equilibria involving diamagnetic metal species

$$M_2 = 2M^+ + 2e^-_{amm}$$

Becker, Lindquist and Alder[69] elaborated upon this theory in order to account for both conductivity and magnetic susceptibility data and introduced the equilibria

$$M = M^+ + e^-_{amm}$$

$$M + M = M_2$$

In this model, the monomer M, consists of an ammoniated M^+ ion with the electron located in an expanded orbital on the protons of the co-ordinated ammonia molecules. The dimer M_2, consists of two ammoniated M^+ ions with the electrons again located in an expanded orbital on the protons of the co-ordinated ammonia molecules. Freed and Sugarman[70] suggested inter-

action of two electrons to form a diamagnetic pair to account for the decrease in paramagnetism. This theory has been elaborated upon by various authors[71-73] who proposed that the individual electrons are trapped in cavities which they create in the solution and are in equilibrium with diamagnetic pairs of electrons which are similarly trapped

$$2e^-_{amm} = e^{2-}_{2amm}$$

The optical absorption spectra of metal-ammonia solutions show a very broad and intense band whose peak occurs at about 15,000 Å.[74,75] The extended short-wavelength tail gives the characteristic blue colour to these solutions. Up to 0.1 M solutions of sodium, potassium, lithium and caesium in liquid ammonia obeys Beer's Law, the spectra being identical for all the metals. This is difficult to reconcile with the proposed models, as it is expected that each species would show different spectral properties. To overcome this, Gold, Jolly and Pitzer[76] assumed that species such as M and M_2 consist of ionic aggregates in which the solvated electrons remain essentially unchanged from their state at infinite dilution.

By adding a third equilibrium to that proposed by Becker, Lindquist and Alder, Arnold and Patterson[77] found better agreement with magnetic and conductivity data. They postulated the existence of two different diamagnetic species. The additional species M^-, consists of an electron trapped in the field of an M centre, and is a negatively charged, diamagnetic entity.

$$M = M^+ + e^-_{amm}$$

$$M_2 = 2M$$

$$M^- = M + e^-_{amm}$$

Jortner[78] has carried out extensive theoretical studies of the energies of bound electrons in liquid ammonia. This work was based on electron binding in ionic crystals but later work[79] was based on a system consisting of a

dielectric medium and the additive electron. His proposal was that in the limiting case of extremely dilute solutions the electron is removed from the metal cation and is located in a cavity in the liquid. The electron is trapped in the medium by self-induced polarisation. This approach gives rather better agreement between predicted properties and experimental values than the other methods outlined.

For the purposes of this work, however, the exact nature of the reducing species is not essential to an understanding of the reduction paths which the organic substrates undergo. The mechanisms of these reductions are discussed in the following section.

2.2. REDUCTIONS IN LIQUID AMMONIA

The earliest theory[80] of reduction was proposed to account for the reduction of unsaturated organic compounds by sodium amalgam in protonic solvents. In this theory it was supposed that the metal reacted initially with the solvent to give hydrogen atoms, which then reacted with the substrate to give the reduction products. Later work[81] showed this to be erroneous, and it was postulated that reduction occurs by addition of sodium atoms to the organic molecule followed by protonation by the solvent. In 1938 Michaelis and Schubert[82] presented the currently accepted reduction mechanism in terms of a reversible one-electron addition as the initial step, followed by protonation and dimerisation or further electron addition and protonation. This theory has now been accepted for reductions by metal-ammonia solutions and it has been possible to formulate two different reaction mechanisms,[83] (A) fission of a saturated bond, and (B) saturation of a double bond, both of which are illustrated below.

(A) Fission of a single bond

Fission of a single bond requires the addition of one or two electrons, the products undergoing one of a number of further reactions. The general

scheme for such reactions is given in Scheme 1.[84]

Direct addition of two electrons may occur, the product anions then existing as such in solution or being protonated by either the ammonia itself if the anions are strong bases or by added proton donors such as ethanol or ammonium salts. Stepwise addition of electrons in the fission of the bond gives rise to a radical and an anion as intermediates after addition of one electron. The anion so formed may be protonated while two possible fates exist for the radical. Radical coupling may occur to give a dimer, with possible further reactions, or the addition of a second electron may occur to give the corresponding anion, which may then undergo further reaction as shown.

For a reaction of this type to occur, the stability of the anions and radicals formed on reduction must be considered; for example, it is to be expected that bonds between electro-negative atoms or between carbon and a very electro-negative atom will be split, particularly if the carbon atom is part of an unsaturated system, e.g., carbon-halogen bonds are readily split with the production of halide ions and organic radicals.

$$-\overset{|}{\underset{|}{C}}-Hal + e^- \rightarrow -\overset{|}{\underset{|}{C}}\cdot + Hal^-$$

(B) Saturation of a double bond

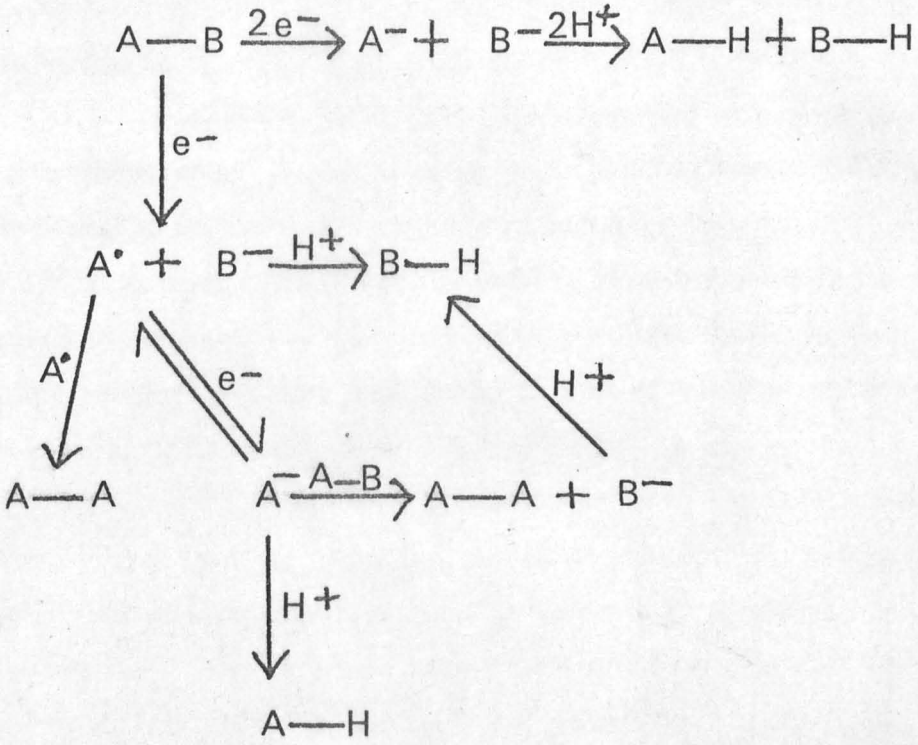
An isolated double bond A = B can be considered as a model for all conjugated systems. As with the fission process, the reduction can involve the simultaneous or stepwise addition of electrons. The general scheme is shown as Scheme 2.[84]

In this case a dianion could be formed by the simultaneous addition of two electrons if the double bond is part of a conjugated unsaturated system where the charges could be stabilised by resonance. One-electron addition may also give a relatively stable radical-anion which resists further reaction,

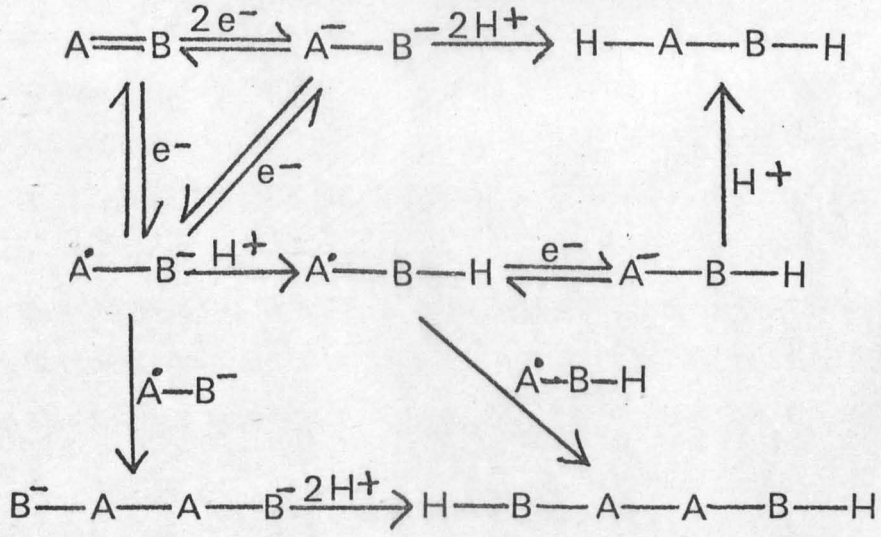
SCHEMES FOR REDUCTION IN LIQUID AMMONIA

Scheme 1 : Fission of a single bond

Scheme 2 : Saturation of a double bond



SCHEME 1



SCHEME 2

or again protonation followed by further electron addition may occur. The radical-anion may dimerise giving the dianion which may then be protonated.

The metal-ammonia solutions permit the reduction of organic materials in a homogenous phase by chemical means. The electrons required for the initial reduction step are produced by the dissolving metals, and the low acidity and relatively high solvating power of ammonia permits the formation and enhances the stability of the radical-anions formed. If the substrate is insoluble in ammonia alone, a cosolvent such as tetrahydrofuran may be added to achieve satisfactory solvent properties.

In many metal-ammonia reductions protonation of anions occurs to give saturated products. Due to the low autoionisation ($pK_a = 34$) of ammonia, a very low concentration of protons is available in ammonia alone. Proton availability may be increased by the addition of substances such as ammonium ions or aliphatic alcohols which behave as strong acids in ammonia.

Reduction of organic compounds in ammonia has also been achieved by electrolysis. Early work on the electrolysis[85] of tetraalkylammonium salts showed the cathode potential to be essentially independent of the cation used. This led to the suggestion that the solvated electron was produced at the cathode and further work[86] showed that the only cathode reaction was a dissolution of electrons into solution. Levy and Myers[64] report that the e.s.r. spectra of electrolysed solutions of tetramethylammonium iodide in ammonia are similar to those of sodium in ammonia, suggesting that both chemical reduction and electrolytic reduction in ammonia occur essentially by the same species and so the paths of reduction in each case should be similar. Electrolytic reductions of a number of species have been reported.[87,88]

CHAPTER 3

EXPERIMENTAL TECHNIQUE

3.1. THE E.S.R. SPECTROMETER

In the e.s.r. spectrometer a klystron oscillator generates a microwave field of frequency 9270.339 Mc. $sec.^{-1}$ which is applied to a resonant cavity containing the sample under investigation. The cavity is situated centrally between the poles of an electromagnet producing a steady static magnetic field of about 3300 oe. and is connected to one arm of a microwave bridge. Before resonance occurs no power is absorbed by the sample, the microwave bridge is balanced and no signal is detected. At resonance, energy is absorbed by the sample from the microwave field and the bridge becomes unbalanced, the imbalance being sensed by a semiconducting crystal detector. Coils in the cavity provide for application of a 100 kc. $sec.^{-1}$ modulating magnetic field. Modulation of the field at resonance causes the e.s.r. information to appear as an alternating current superimposed on the microwave energy reflected from the cavity to the detector. This allows phase detection and, after amplification, the resultant e.s.r. signal, appearing as the first derivative of the absorption curve, is applied to an oscilloscope or graphic recorder. In order to traverse the whole absorption, a small sweep field is superimposed on the steady magnetic field. This allows the detection of absorption which can be spread over tens of oersteds for organic radicals.

The spectrometer used in this work was a Decca X1 model with a Newport Instruments 7 inch magnet system and employing 100 kc. $sec.^{-1}$ frequency modulation.

3.2. THE MULTICAPILLARY MIXING CHAMBER

The essential feature of a flow system is the mixing chamber. For accurate and reproducible results mixing must be fast and efficient. This is

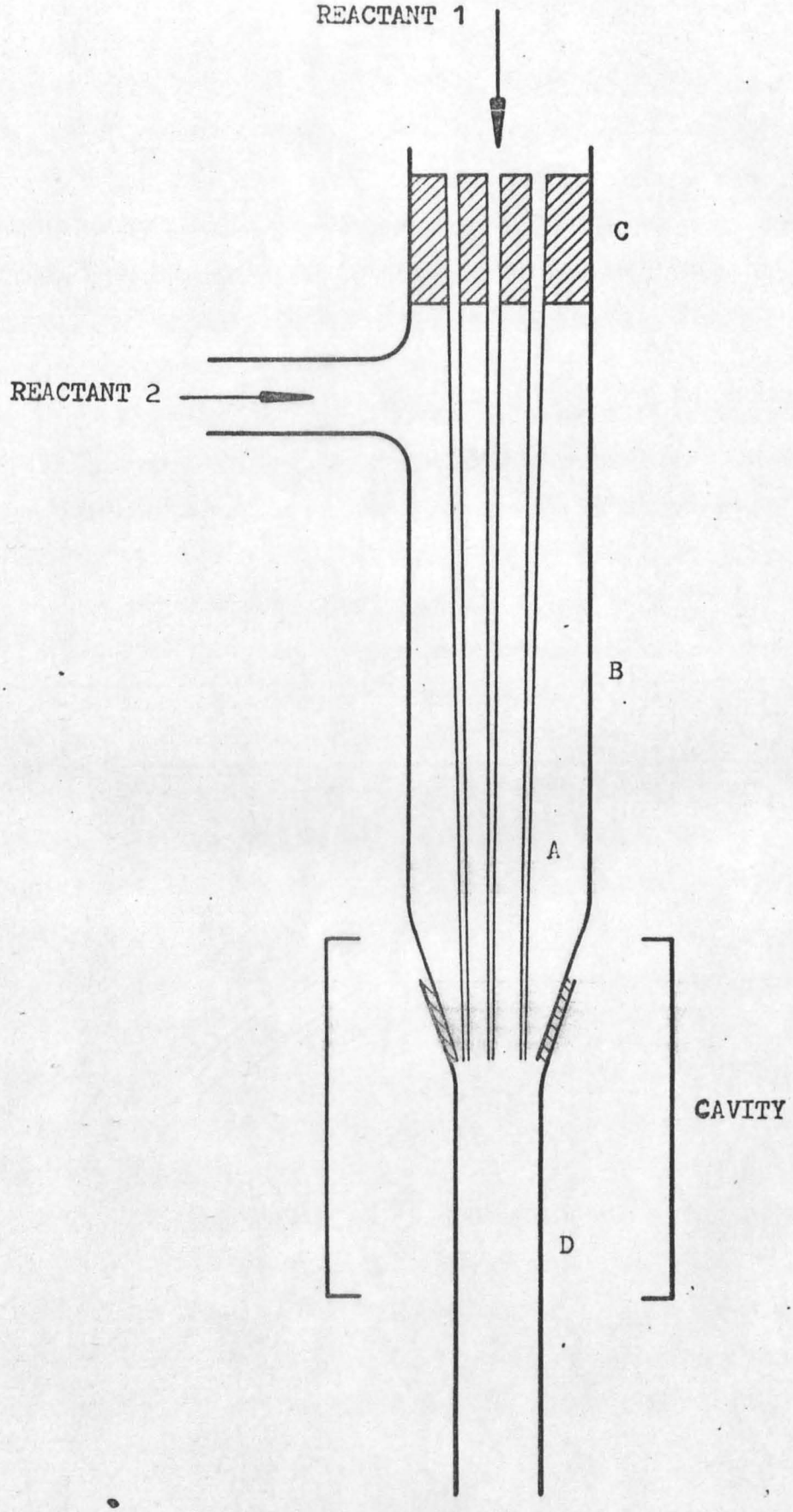
particularly so with e.s.r. studies, as inefficient mixing can lead to broadening of the hyperfine lines of the e.s.r. spectrum and hence to a lowering of resolution.

Flow systems used in e.s.r. studies have been based on the designs first described by Hartridge and Roughton.[89] In these systems the mixing chambers have been adapted in numerous ways to suit the experimental conditions. They range from the very simple system used for detecting the relatively stable p-benzosemiquinones,[6] through designs to reduce the dead-space[90] inherent in the mixers to the more complex designs used for reactions in biological systems.[91]

The conventional mixing chamber[51,57] used in previous e.s.r. work incorporates a time-lag between mixing and observation which is too large for certain of the radicals reported in this work to be observed. The dead-space is about 0.1 $cm.^3$ and with a maximum flow rate of 5 $ml.sec.^{-1}$, observation can be made 0.02 sec. after mixing. A mixing chamber has been developed in which mixing occurs much closer to the centre of the resonant cavity and where observations may be made 2 - 5 msec. after mixing.

The cell used is shown in the figure. It is a considerably modified version of the multicapillary mixer of Moskowitz and Bowman.[92] Contained within the outer glass jacket (B) (ca. 6 mm. i.d. at top and 2 mm. i.d. at the mixing point) is a bundle of 10 - 20 capillaries (A) (ca. 0.5 mm. i.d.). These are held in place at the top by Araldite (C). The mixer is constructed in the following way. The jacket is blown to the required shape and size and the end pulled down to a nozzle. The capillaries are drawn to the required length and diameter, and inserted into the jacket, as many being packed in as possible. The ends of the capillary tubes at the top of the mixer are then flame sealed and the mixer inserted into liquid Araldite until it reaches the level of the side arm. This is allowed to stand for 24 hours, when the Araldite is firmly set, and the end cut off with a diamond saw. The nozzle is then sawn off at the correct diameter and the observation tube (D) fixed,

MULTICAPILLARY MIXING CHAMBER


REACTANT 1
C
REACTANT 2
B
A
CAVITY
D

again with Araldite. The relatively low dielectric constant of ammonia (22 at -33°C) permits the use of 2.4 mm. i.d. tubing as sample cell.

Mixing is complete within 2 - 3 mm. of the nozzle (as evidenced by runs with acids, bases and indicators, and also the ammonia solutions) indicating a dead-space of about 0.01 $cm.^3$ At the fastest flow rates of about 8 $ml.sec.^{-1}$, complete mixing is effected within 2 msec., although such large flow rates were not generally required.

Comparative experiments between the aqueous solution-type mixer used previously and the multicapillary mixer described above showed, where spectra were obtained in both cases, that the multicapillary mixer gave better signal-to-noise ratios and, in most cases, higher resolution. This type of mixer allows observations on radicals with half lives an order of magnitude lower than those obtained by the aqeuous solution mixer.

3.3. TYPICAL PROCEDURE

Each solution was contained in a 2 l. round-bottomed flask, cooled with solid carbon dioxide ("Drikold"). The solution of sodium in liquid ammonia was forced under pressure of nitrogen through the side arm of the mixer and down the interstices, a solution of the substrate under investigation being similarly forced through the capillaries. All flow tubes were cooled with "Drikold" throughout each run and the products collected in a cooled 5 l. flask. The cavity was surrounded by a polythene bag through which a constant stream of nitrogen was passed to prevent icing and consequent loss of resolution. No cooling of the cavity was necessary.

Distilled anhydrous ammonia, purchased from I.C.I. Limited in 283 lb. (88 lb. ammonia) cylinders and quoted to be 99.98% pure, was not further purified. Before adding the substrate or reductant to the ammonia, small pieces of clean metallic sodium were added, initially giving a deep blue colour. Any impurities cause decoloration of the solution and when a very

faint, permanent blue colour remained, the required amounts of substrate and reductant were added. The substrate solution was made up to a concentration of 10^{-3} - 10^{-2}M, the concentration of reductant being normally slightly greater. In cases where the substrate was only partially soluble in ammonia alone, purified tetrahydrofuran was used as a cosolvent (ca. 5% v/v). Runs were normally performed with 2 l. of each solution and at the fast flow rates employed, the large consumption permitted spectra to be run with a maximum magnetic field sweep time of only 500 sec. Consequently the resolution of the spectra is inherently lower than would be expected from a static system.

Experiments permitting observation of secondary radicals were carried out by allowing mixing to occur up to 1 sec. before the cavity, and static observations gave the e.s.r. spectra of any paramagnetic products. The static experiments were conducted by adding a few milligrams of substrate to a 0.5 M solution of sodium in ammonia, maintained at about -60° C. The mixture was rapidly transferred to a variable temperature assembly in the spectrometer cavity, and spectra run about 2 min. after mixing. The electron signal was invariably always present initially, but on stirring this disappeared to be replaced by a more complex spectrum if paramagnetic species existed. No special effort was made to exclude air but the blueness of the mixed solution and the strong signal due to e^-_{solv} is reasonable guarantee of the absence of oxygen.

3.4. RECORDING OF SPECTRA

The basic procedure for operating an e.s.r. spectrometer is very varied and depends upon the instrument itself, and will not be considered here. A number of precautions, however, should be noted in order to obtain the best spectrum from a free radical sample. With some easily saturated systems, too high a microwave power level will cause decrease in signal intensity and resolution due to line broadening.[93] Low power levels should therefore be

used, though not too low to prevent sufficient signal intensity. The modulation amplitude should be as low as possible to avoid line broadening[93] which obscures much of the fine detail in spectra. The sample should not display too much dielectric "loss" and should be placed in the centre of the cavity so that it experiences the greatest microwave magnetic field density and least electric field density. The cavity itself should be in the position of maximum field homogeneity. A low concentration of radicals is preferable to prevent spin-spin broadening. Also, distortion of the line shape will occur if the magnetic field is swept rapidly, so a slow sweep speed should be used if possible.

With a flow system such as that described above, all the conditions for obtaining good spectra cannot be realised. The available parameters must be optimised to obtain the best possible spectrum. In all cases, relatively short magnetic field sweep times have to be used, and this is balanced to some extent by a relatively high modulation amplitude to give satisfactory signal size.

In all cases the magnetic field was calibrated using a dilute alkaline solution of potassium nitrosyl disulphonate (Frémy's salt). The radical dianion $\cdot NO(SO_3)_2^{2-}$ is produced and gives a three line spectrum, of relative intensities 1 :1 :1, the lines being separated by 13.07 Oe. Determination of the coupling constant of Frémy's salt was made by averaging a number of runs in which the magnetic field was plotted directly along the X-axis of an X - Y recorder. Cross-checking of coupling constants was also carried out occasionally with the perylene radical-cation (obtained from a solution of perylene in concentrated sulphuric acid).

Calibrations were always carried out on the same day as the samples were run, and the average value of a number of scans taken. The quoted coupling constants for all radicals were obtained from an average of several spectra, where possible, and are estimated to be accurate to 0.03 Oe.

The solvated electron gives a single, narrow line with a g-value of 2.0011,[94] and centred at a field-value, for this work, of 3310 Oe. By taking

the e.s.r. spectra of Frémy's salt, diphenylpicrylhydrazyl (DPPH) and sodium in ammonia simultaneously, the g-value of the solvated electron can be calculated, as those of Frémy's salt and DPPH are known. As the microwave frequency is known (9270.339 Mc.sec.$^{-1}$), and the values of Plank's constant and the Bohr magneton, the field-value can be calculated from equation (4).

Assuming the g-value for the solvated electron to stay constant in the presence of other radicals, the g-values for these radicals may be directly determined from

$$g_{rad} = \frac{g_e H_e}{H_e - x}$$

where g_{rad} and g_e are the g-values of the radical and solvated electron respectively, H_e is the field-value of the solvated electron, and x is the distance, measured in oersteds, of the centre of the spectrum of the radical downfield from the solvated electron line. All g-values quoted have been determined on this basis, and are estimated to be accurate to 0.0001.

CHAPTER 4

REDUCTION OF ARYL HALIDES

4.1. INTRODUCTION

The high electronegativity of the halogens renders the carbon-halogen bond highly susceptible to cleavage by metal-ammonia solutions, the halogen being cleaved as halide ion. However, other factors such as bond energy will be important in determining the ease of cleavage of the bond, and the relatively high carbon-fluorine bond energy[95] probably accounts for the fact that only species containing fluorine show halogen splitting on one-electron reduction on the time-scale of our measurements. Chablay[96] first demonstrated the reaction but made no product analysis. Fluorides excepted, alkyl halides,[96-98] aryl halides,[99, 100] and polyhalogenated benzenes[101] lose halogen on reaction with sodium in ammonia; for example, chlorobenzene gives benzene, diphenylamine, triphenylamine and sodium chloride, and 1-iodonaphthalene gives naphthalene.[102] Cleavage of a variety of benzyl halides gives a mixture of the corresponding alkane and bibenzyl.[103]

Dehalogenation of organic halogeno compounds has also been studied by (i) ultraviolet and gamma-irradiation of alkyl and aryl halides,[31, 104-108] (ii) electron transfer from (a) lithium metal in diethylether to chloro-substituted naphthalenes,[109] (b) sodium naphthalenide to alkyl halides,[110] (c) sodium atoms to phenyl iodide,[111] (d) the radicals $\cdot CO_2^-$ or $\cdot CO_2H$ generated from formic acid in titanous-hydrogen peroxide systems to alkyl halides,[54] and (iii) by reaction between lithium alkyls and alkyl halides.[112] E.s.r. studies were made in some of these cases[31, 54, 105, 106, 109] but poorly resolved spectra were obtained except in liquid solution.[58, 109] Analogous studies[111] of aromatic halides are few and e.s.r. spectra are normally obtained only when the substrate contains a strong electron-withdrawing group. The radical-anions of the fluoro-[113-115] and chloro-[113] nitrobenzenes exhibit splitting due to the halogen atoms, and interaction of the fluorine nucleus is also apparent in the radical-anions of p-fluoroacetophenone[63] and 2,7-difluorofluorenone,[116] the

fluoranil semiquinone[117] and certain fluorobiphenyls.[118] Irradiation of single crystals of mono-[119] and tri-[120] fluoroacetamide gives e.s.r. spectra showing fluorine splittings.

Nuclear halogen atoms are readily removed from nitrogen heterocyclic rings catalytically[121] and with zinc dust in acid or alkali,[122] and dehalogenation of some chloroimidazopyridazines has been observed on treatment with sodium in liquid ammonia.[123]

A study of the reduction of aryl halides was undertaken, utilising the fast mixing device and flow system described in Chapter 3, in an attempt to observe the aryl halide radical-anions first formed on reduction. Altogether twenty-seven examples of ring-halogenated pyridine, pyrimidine, benzene, biphenyl, naphthalene and benzonitrile were examined and the results are presented below. Halogenated benzoic acids have also been examined and the data are presented in Chapter 6.

4.2. EXPERIMENTAL

Substrate concentrations were made up to 10^{-3} - 10^{-2} M, the individual concentrations depending on optimum signal size and resolution, and a slight excess of sodium was normally used. In the cases of 2,3- and 3,5-dichloropyridines, 2,2'-difluorobiphenyl, 1-iodonaphthalene and 4-iodotoluene, ammonia with 10% v/v of purified tetrahydrofuran as cosolvent was used to obtain satisfactory solvent properties, otherwise liquid ammonia was used alone.

Maximum flow rates of ca. 8 ml. $sec.^{-1}$ were used in every case, but when the radical-anion of the parent compound was the only one observed, lower flow rates provided comparable spectra. Spectra were also run in some cases with mixing occurring ca. 0.1 and 1.0 sec. before the cavity, to allow observation of any secondary radicals which may have been formed.

Materials

The anhydrous ammonia was used without purification further than that indicated previously. Sodium was carefully washed with light paraffin

oil and dried immediately before use. All the halides were commercial products and were purified, if necessary, by recrystallisation or distillation.

Iodobenzene

Commercial iodobenzene contains 0.5 - 1% nitrobenzene (determined by G.L.C.) and when this material was used at 5×10^{-3} M, the e.s.r. spectrum obtained was identical to that of the nitrobenzene radical-anion. Iodobenzene was therefore prepared by the method of Barker and Waters[124] to ensure the complete absence of nitro-compounds (B.Pt. = 29 - 30° at 0.5 mm). G.L.C. showed it to be free of nitrobenzene.

4.3. RESULTS AND ANALYSIS OF SPECTRA

The coupling constants obtained from a number of mono- and di-halogen substituted aromatic hydrocarbons and nitrogen heterocycles are listed in Table 4.1.

4.3.1. Halogenated pyridines and pyrimidines

All the pyridines (with the exception of 2-fluoropyridine) and two pyrimidines gave the e.s.r. spectrum of the radical-anion of the parent heterocycle. The coupling constants are in close agreement with those of Talcott and Myers[66] who obtained the anions of the unsubstituted heterocycles by electrolytic reduction in ammonia. The e.s.r. spectrum obtained from 3-iodopyridine is shown in Figure 4.1. 2,4,6-Trichloropyrimidine was reduced under similar conditions to the two dichloro-compounds, but no e.s.r. spectrum could be detected.

Fluoro-substituted pyridine behaves quite differently from the other halogenated pyridines. 2-Fluoropyridine retains the fluorine atom on reduction, because the e.s.r. spectrum of the radical-anion shows 82 lines, the larger proportion of which are of equal intensity. The number of lines expected from a pyridine nucleus substituted with an atom of spin 1/2 in the 2-position is 96 if no simple relationship exists between the coupling constants; hence if overlap is allowed for, the spectrum can be rationalised in terms of

TABLE 4.1.

COUPLING CONSTANTS FOR RADICAL ANIONS PRODUCED FROM SUBSTITUTED COMPOUNDS

Substrate	Radical-anion	Coupling Constants (oersteds) a_1[a]	a_2, a_6	a_3, a_5	a_4
2-Fluoro-pyridine	2-fluoro-pyridine	4.82	7.12,[b] 4.62	3.67, 1.67[c]	8.31
2-Bromo-pyridine	pyridine	6.26	3.54	0.82	9.54
2-Chloro-pyridine[d]		6.5	3.7	0.8	9.9
3-Chloro-pyridine		6.30	3.35	0.81	9.63
3-Iodopyridine		6.33	3.55	0.81	9.66
2,3-Dichloro-pyridine[d]		6.3	3.4	0.8	9.6
2,6-Dichloro-pyridine		6.30	3.54	0.83	9.72
3,5-Dichloro-pyridine		6.18	3.49	0.78	9.58
2,6-Dibromo-pyridine		6.23	3.50	0.78	9.54
Pyridine	pyridine[e]	6.28	3.55	0.82	9.70
2,4-Dichloro-pyrimidine[d]	pyrimidine	3.3[f]	0.7[g]	1.3[h]	9.9[i]
4,6-Dichloro-pyrimidine	pyrimidine	3.27[f]	0.75[g]	1.33[h]	9.82[i]
Pyrimidine	pyrimidine[e]	3.26[f]	0.72[g]	1.31[h]	9.78[i]
Iodobenzene	biphenyl		2.72	0.40	5.44
4-Diiodobenzene			2.70	0.40	5.41
2-Iodobiphenyl			2.70	0.38	5.40

.....continued

Substrate	Radical-anion	Coupling Constants (oersteds)					
		a_1[a]	a_2	a_6	$a_{3'}$	a_5	a_4
Biphenyl	biphenyl[j]		2.73		0.43		5.46
2,2'-Difluoro-biphenyl	2,2'-difluoro-biphenyl		3.78,[b]	3.25	0.35	0.73[k]	5.84
1-Iodonaphthalene	naphthalene		5.02,[l]	1.85[m]			
Naphthalene	naphthalene[n]		5.01,[l]	1.79[m]			

[a] a_N.

[b] Probably a_F.

[c] MO calculation ambiguous

[d] Spectra not very well resolved, so the coupling constants are open to larger errors.

[e] Values from Ref. 33.

[f] a_1, a_3.

[g] a_2.

[h] a_5.

[i] a_4, a_6.

[j] In THF or DME; values from A. Carrington and J. dos Santos-Veiga, Mol. Phys. 1962, 5, 21.

[k] MO calculations predict $\rho_5 > \rho_3$; therefore on this assumption $a_5 = 0.73$ oe. and $a_3 = 0.35$ oe.

[l] a_1, a_4, a_5, a_8.

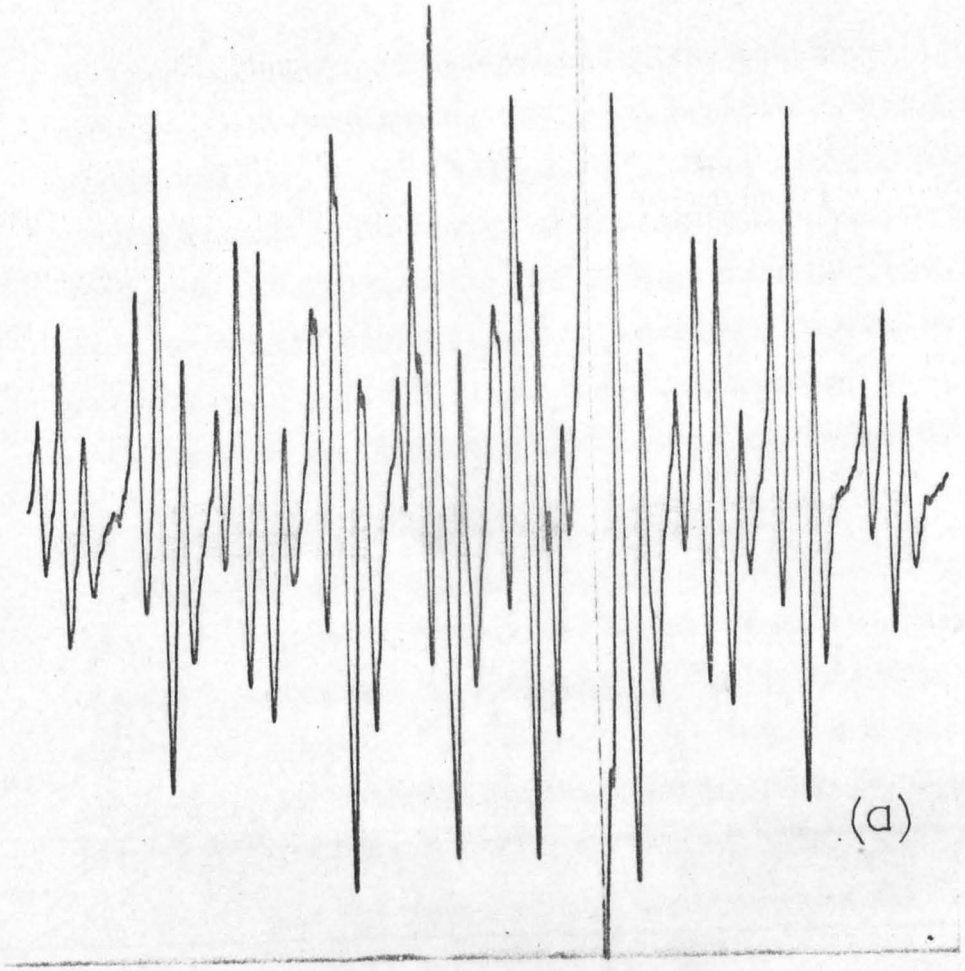
[m] a_2, a_3.

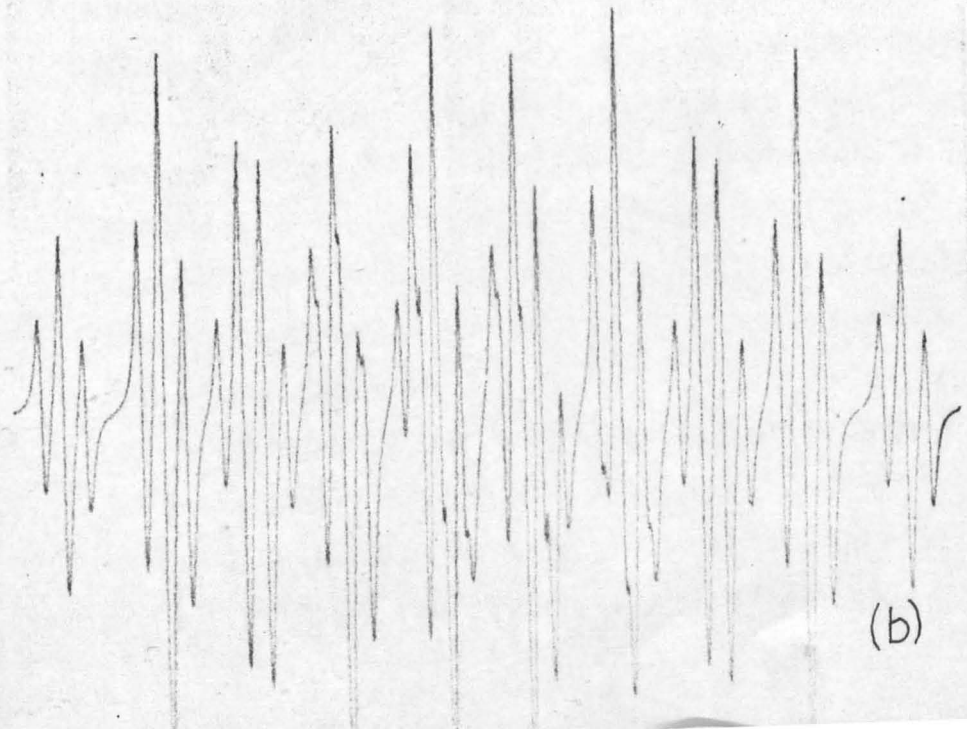
[n] In THF or DME; values from T. R. Tuttle, R. L. Ward and S.I. Weissman, J.C.P. 1956, 25, 189.

FIGURE 4.1.

(a) Spectrum from 3-iodopyridine

(b) Computer simulated spectrum


(a)


(b)

$C_5H_4NF^{\cdot-}$. Imposition of a 1.0 sec. delay between mixing and observation left the spectrum unchanged. The coupling constants are given in Table 4.1 and the spectrum is shown in Figure 4.2. Static experiments were also performed with this substrate and the e.s.r. spectrum obtained a few minutes after mixing is highly complex, and although a complete analysis has not been made, it would appear from the very low nitrogen coupling constant of ca. 0.3 oersted that the 4,4'-dimer is not formed. Assignment of the coupling constants is discussed below. The g-value for the monomer radical-anion is 2.0020.

4.3.2. Halogenated aromatic hydrocarbons

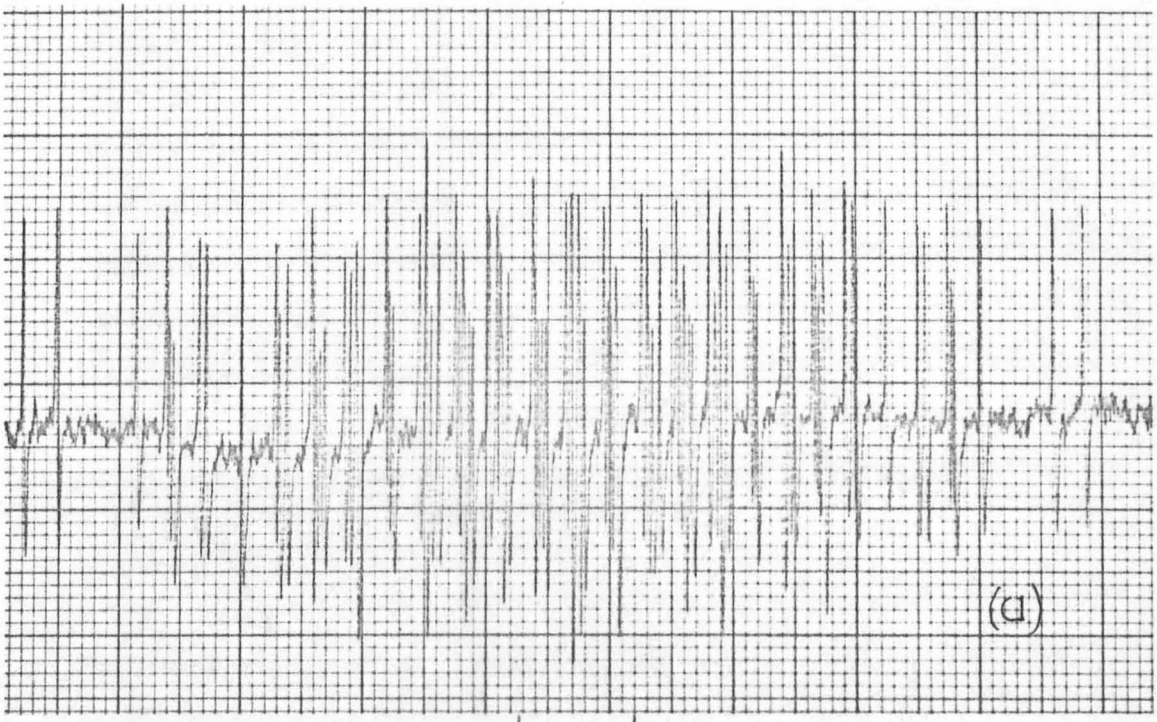
Reductions of 1-iodonaphthalene and 2-iodobiphenyl gave the e.s.r. spectrum of the radical-anion of the parent hydrocarbon. In these cases the coupling constants must be compared with those previously obtained in ethereal solvents and ammonia[125] (see Table 4.1). Reduction of commercially obtained iodobenzene gave an e.s.r. spectrum identical to that obtained on reduction of nitrobenzene (with coupling constants a_N 11.3; $a_{2,6}$ 3.4; $a_{3,5}$ 1.1; a_4 3.8 oersted). The purity of the iodobenzene was checked by gas-liquid chromatography and it was found to contain 0.5 - 1% of nitrobenzene. When this material was used at 5×10^{-3} M (i.e. with $[C_6H_5NO_2] \sim 5 \times 10^{-5}$ M) the spectrum obtained was that of $C_6H_5NO_2^{\cdot-}$, whereas reduction of iodobenzene prepared by the method described previously gave a low intensity e.s.r. spectrum identical to that of the biphenylide ion. This suggests that an electron-transfer from biphenylide ion to the nitrobenzene impurity may be taking place. The biphenylide ion spectrum was also obtained from 4-diiodobenzene, although reduction of bromobenzene, 2-diiodobenzene and 4-chloroiodobenzene gave no detectable signal. Ill-resolved spectra were obtained from 3- and 4-iodotoluene.

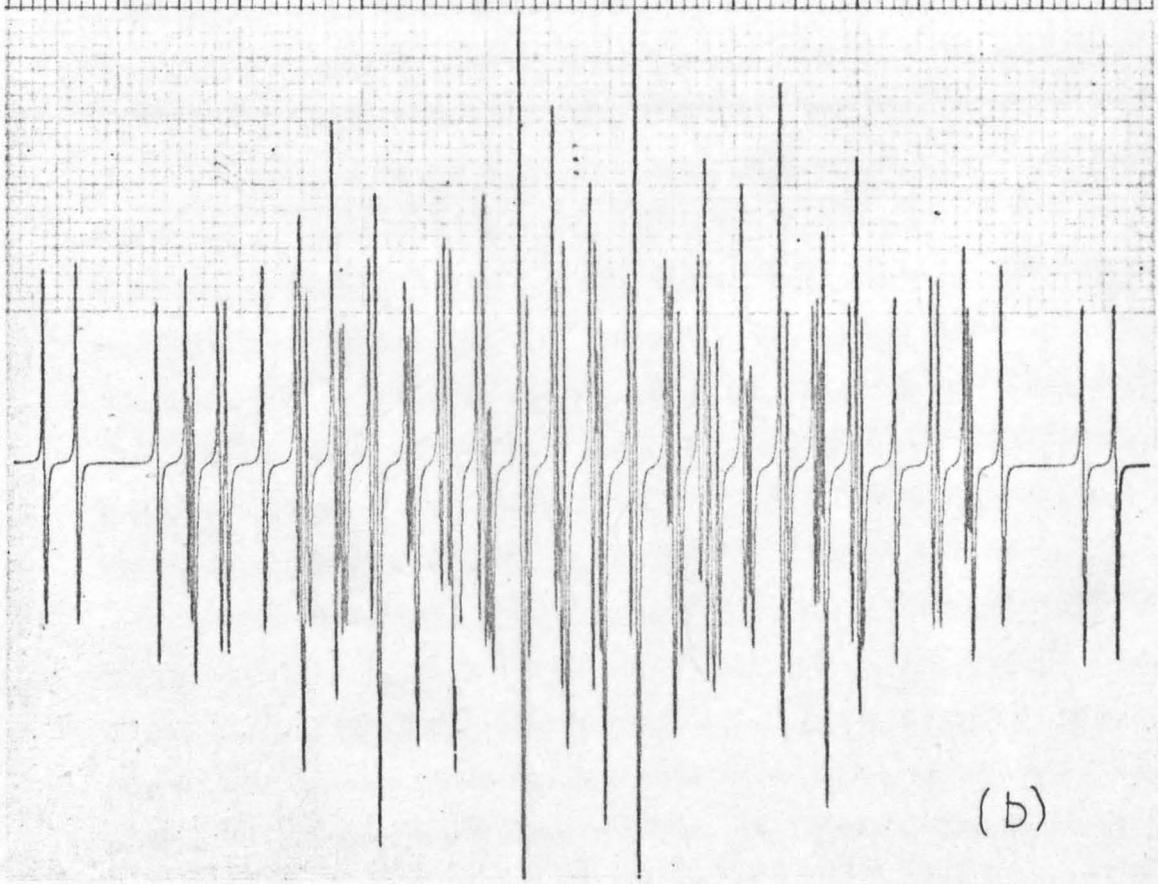
2,2'-difluorobiphenyl gave a complex spectrum on reduction, which can be analysed in terms of five non-equivalent 1 :2 :1 triplet splittings. This could only arise if the fluorine atoms remained attached to the molecule giving an unsymmetrical charge distribution. The coupling constants are

FIGURE 4.2.

(a) Spectrum from 2-fluoropyridine

(b) Computer simulated spectrum


(a)


(b)

given in Table 4.1 and the spectrum in Figure 4.3. Superimposed on the main signal is a very much smaller one due to the biphenyl radical-anion. By employing a twentyfold excess of sodium, or by allowing mixing to occur 1.0 sec. before the cavity, it was possible to enhance the biphenylide ion signal to the complete exclusion of the difluorobiphenylide. Discussion of the assignment of the coupling constants is given below. The g-value for the radical is 2.0031. 4-fluorobiphenyl gave a small, poorly-resolved spectrum for which no analysis could be made, although it appears to be unlike the biphenylide spectrum, suggesting the retention of the fluorine atom.

4.3.3. Halogenated benzonitriles

Using the rapid-mixing technique the e.s.r. spectra of the three monofluoro-substituted benzonitriles have been obtained. The benzonitrile radical-anion alone was observed with 2- and 4-chlorobenzonitriles, while pentafluorobenzonitrile gave a very small and uninterpretable spectrum. The coupling constants are given in Table 4.2.

Analysis of the spectra from 2- and 3-fluorobenzonitrile was tedious but straightforward, splitting from a single nitrogen atom and five non-equivalent nuclei, each with spin 1/2, being obtained in each case. The spectrum obtained from o-fluorobenzonitrile is shown in Figure 4.4. The spectrum from the reduction of 4-fluorobenzonitrile presented a much more difficult problem, as the wings exhibit different splitting patterns, as can be seen in Figure 4.5a. This asymmetry suggests the presence of two radicals, and the spectrum can be analysed in terms of two species, the spectra being separated by 0.55 oe. In each case, splitting from a single nitrogen nucleus, two groups of two equivalent protons and a single nucleus of spin 1/2 was observed. By imposing a 1.0 sec. delay between mixing and observation, the spectrum shown in Figure 4.6a was obtained, and can be analysed in terms of one radical only, the unsubstituted benzonitrile anion, with coupling constants in close agreement with those previously obtained[126] (Table 4.2.). The first spectrum can now be analysed as a combination of

TABLE 4.2.

COUPLING CONSTANTS FOR THE HALOBENZONITRILE RADICAL-ANIONS

Benzonitrile	Position	Coupling Constant (oe)	Spin Densities	Calculated Spin Densities		g-values
				Hückel	McLachlan	
2-fluoro	N	2.17		0.116	0.120	2.0029
	F	5.54	0.111	0.104	0.103	
	3	0.47	0.020	0.048	-0.007	
	4	9.14	0.387	0.252	0.333	
	5	1.11	0.047	0.037	-0.024	
	6	3.41	0.144	0.119	0.127	
3-fluoro	N	2.26		0.117	0.121	2.0028
	F	2.51	0.005	0.039	-0.021	
	2	4.74	0.201	0.118	0.125	
	4	7.87	0.333	0.249	0.329	
	5	0.57	0.024	0.044	-0.013	
	6	2.94	0.125	0.107	0.108	
4-fluoro	N	2.08		0.117	0.121	2.0031
	F	22.96	0.459	0.249	0.326	
	2, 6	4.38	0.186	0.116	0.118	
	3, 5	0.84	0.036	0.039	-0.019	
Unsubstituted	N	2.19		0.117	0.121	2.0028
	2, 6	3.82	0.162	0.112	0.115	
	3, 5	0.32	0.001	0.042	-0.017	
	4	8.52	0.361	0.252	0.332	

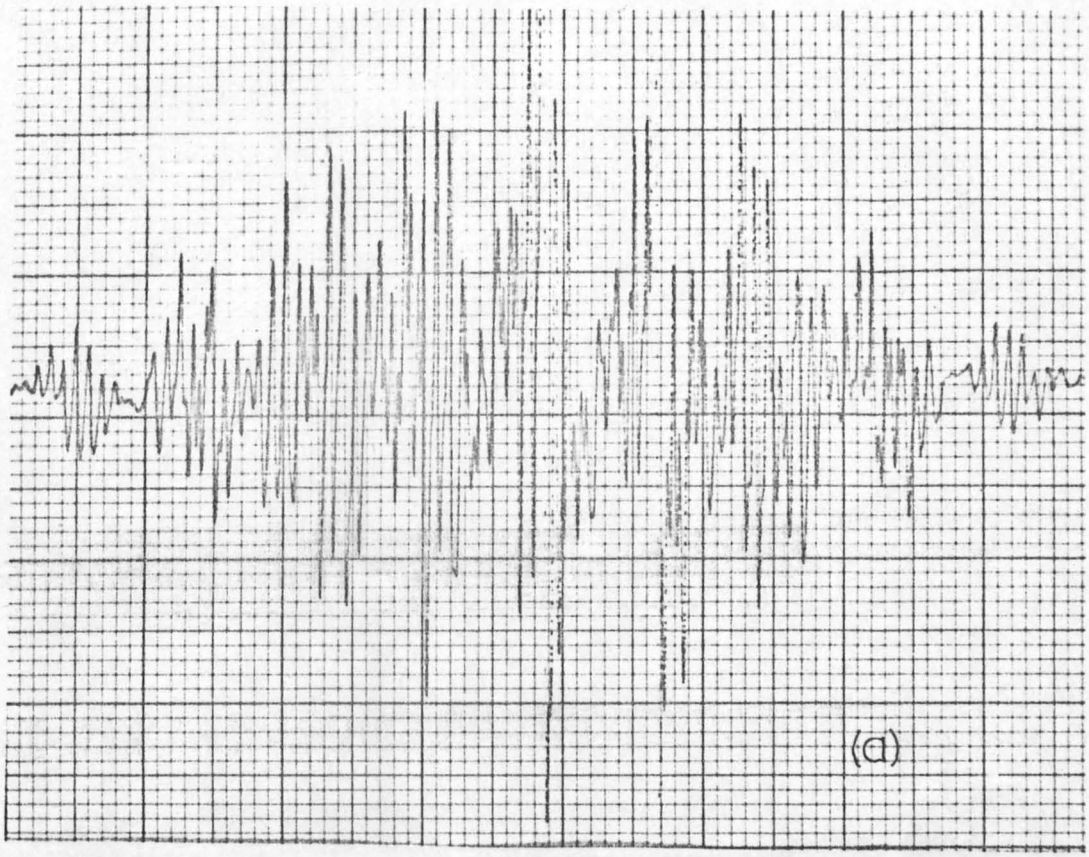
	Position			
	N	2	3	4
Unsubstituted[a]	2.15	3.63	0.30	8.42
2-chloro	2.16	3.83	0.31	8.50
4-chloro	2.13	3.80	0.34	8.44

[a] In DMF ; from ref. 35.

FIGURE 4.3.

(a) Spectrum from 2,2'-difluorobiphenyl

(b) Computer simulated spectrum


(a)

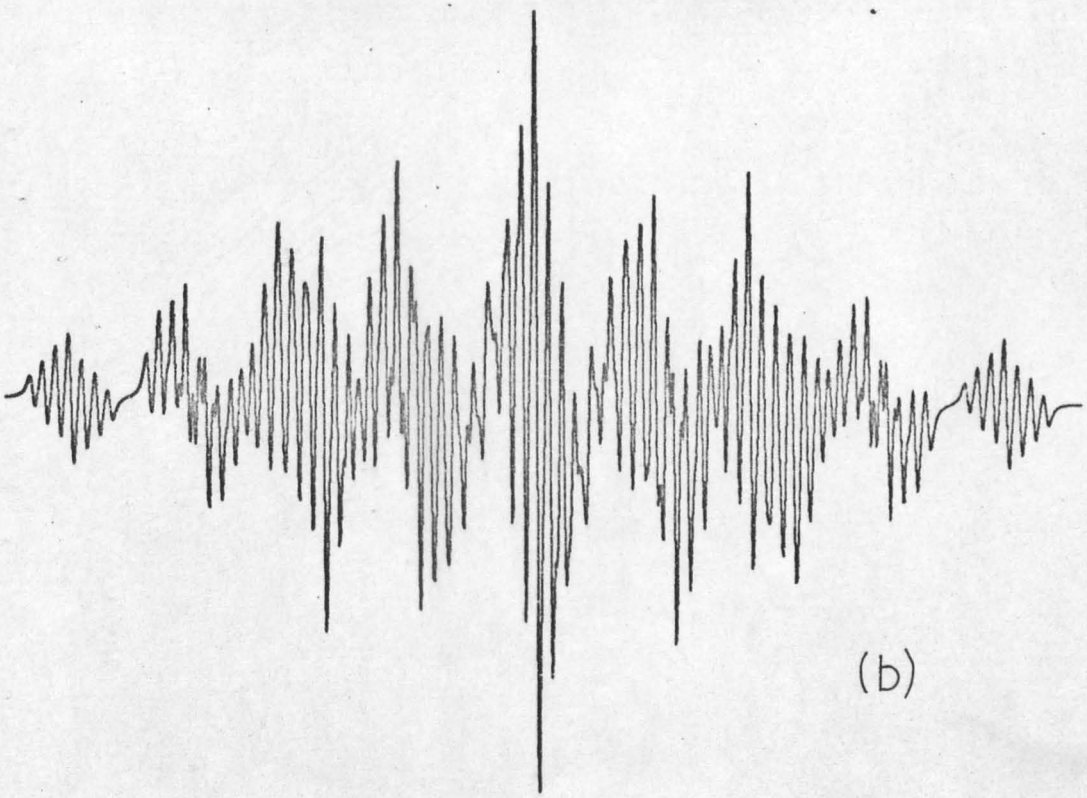
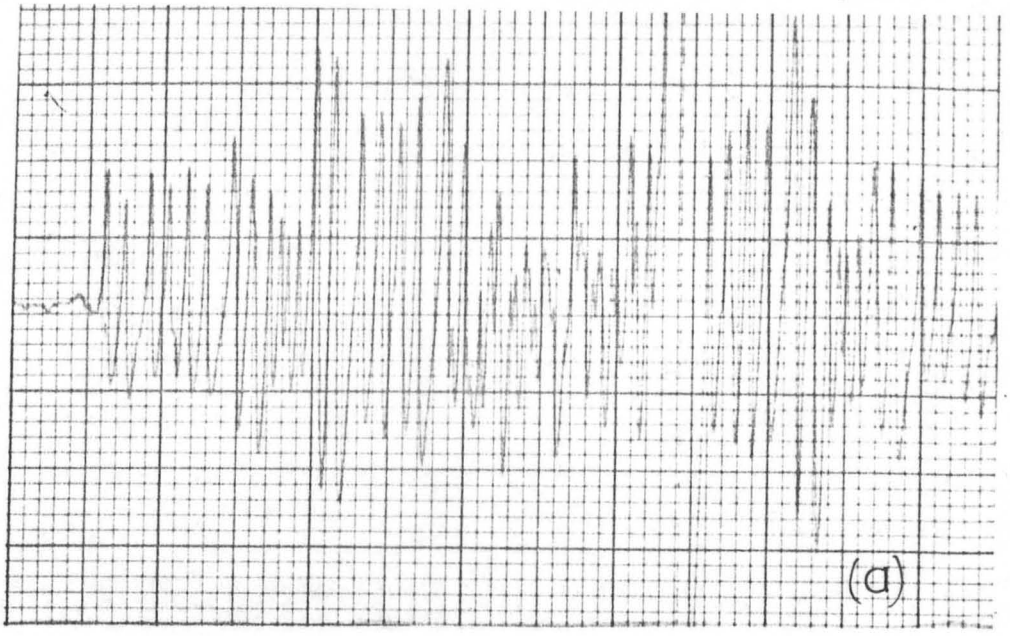

(b)

FIGURE 4.4.

(a) Spectrum from 2-fluorobenzonitrile

(b) Computer simulated spectrum

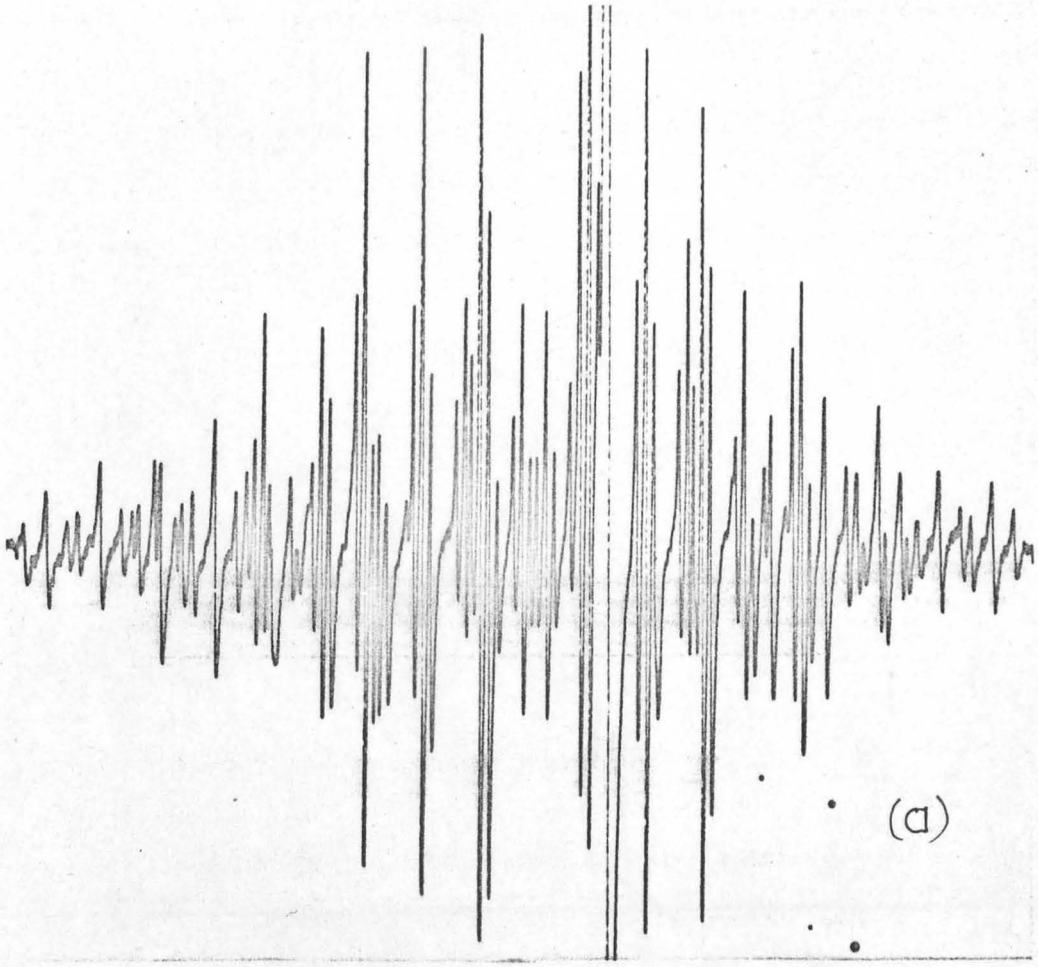

(a)


(b)

FIGURE 4.5.

(a) Mixed spectrum from 4-fluorobenzonitrile

(b) Computer simulated mixed spectrum


(a)

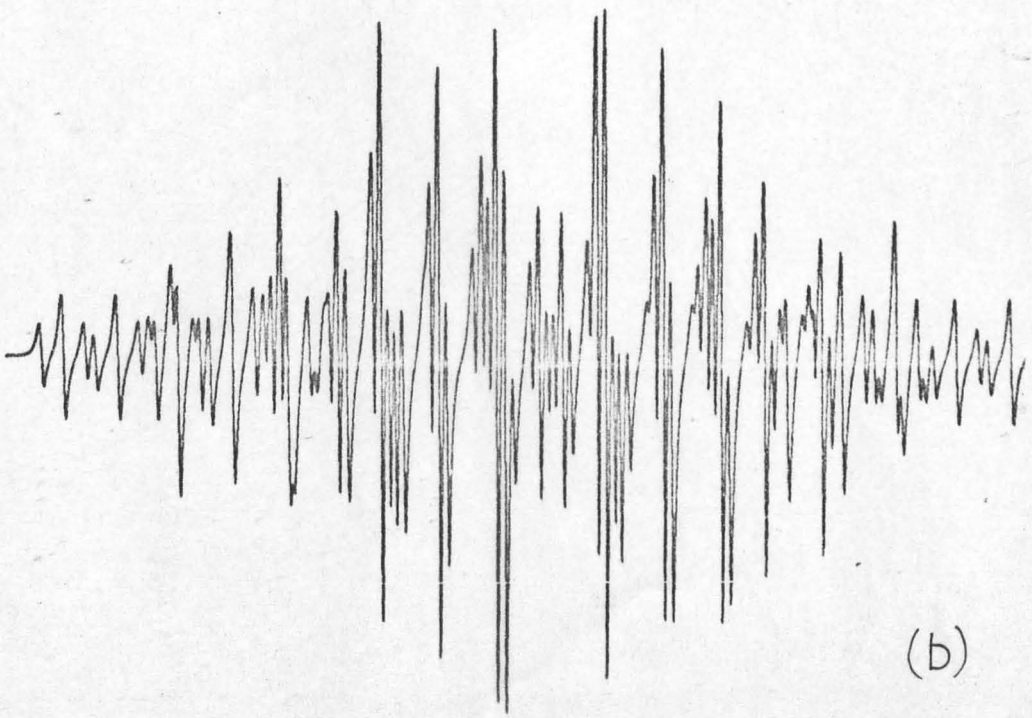
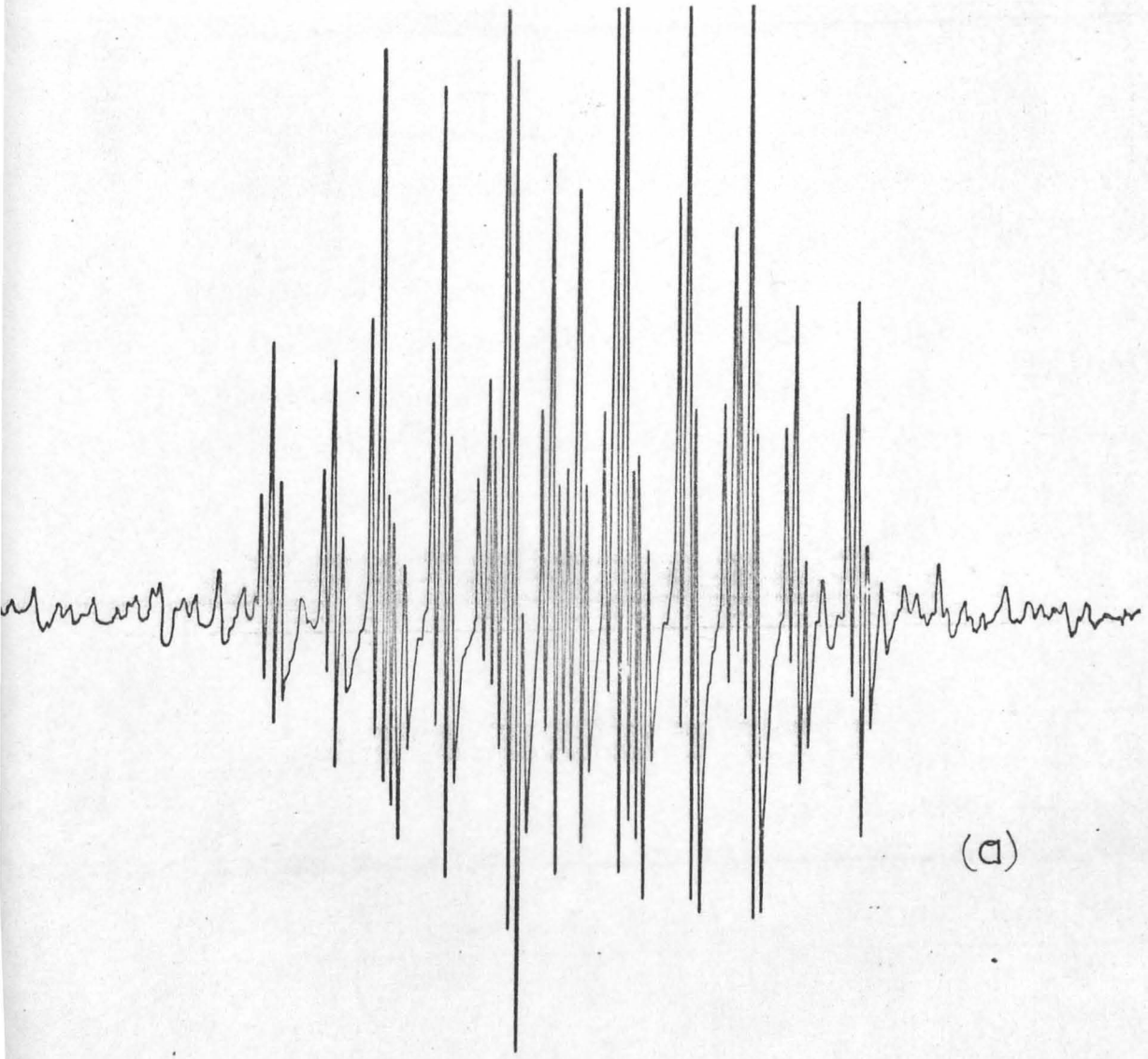

(b)

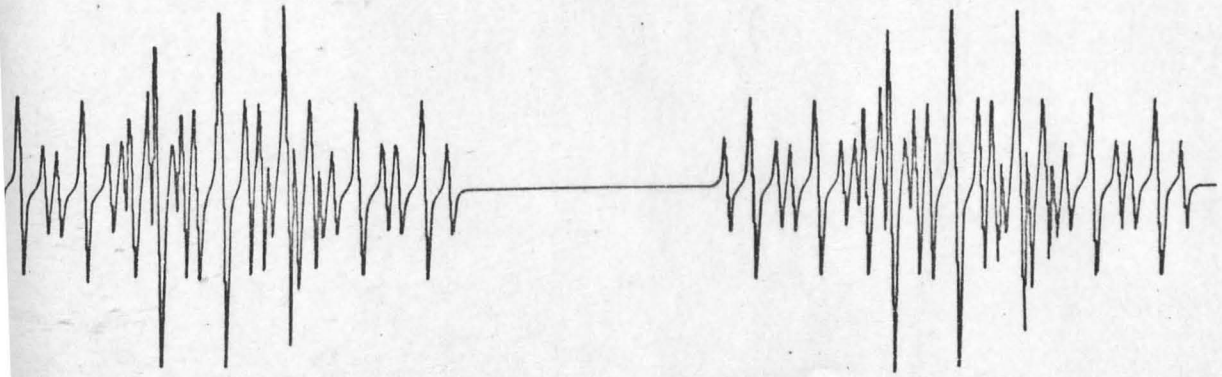
FIGURE 4.6.

(a) Spectrum of benzonitrile

(b) Computer simulated spectrum of 4-fluorobenzonitrile



(a)



(b)

the benzonitrile radical-anion and the 4-fluorobenzonitrile radical-anion, with the coupling constants shown in Table 4.2. The computer simulation of the mixed spectrum is shown in Figure 4.5b. and that of the 4-fluorobenzonitrile radical-anion in Figure 4.6b.

The unsubstituted benzonitrile radical-anion was also obtained from 2-fluorobenzonitrile if observation was delayed for 1.0 sec. after mixing, but it could not be obtained at all from 3-fluorobenzonitrile. A discussion of the assignment of coupling constants to particular ring positions is found below.

4.4. DISCUSSION

Reduction of monohalogenated aromatic compounds with alkali metals in liquid ammonia has been shown to proceed rapidly and efficiently. Although no direct evidence for the mechanism in this type of reduction has been obtained, it has been postulated on the basis of data from the results of competitive reactions and from isotope effects[99] that the first step is the rapid reversible addition of one electron to the aromatic nucleus to form a radical-anion. This species is then protonated by a molecule of solvent, or by a stronger acid if present, in the rate determining step. The rapid attachment of a second electron and loss of halide ion follows.

Second-order rate constants for the reaction of e^-_{aq} with some of the substrates used in this work have been previously measured[127] indicating the occurrence of an initial, fast electron addition.

Substrate	PhCN	PhBr	PhI
$10^{-9} k_2$ (l.mole^{-1} sec.$^{-1}$)	16	4.3	12

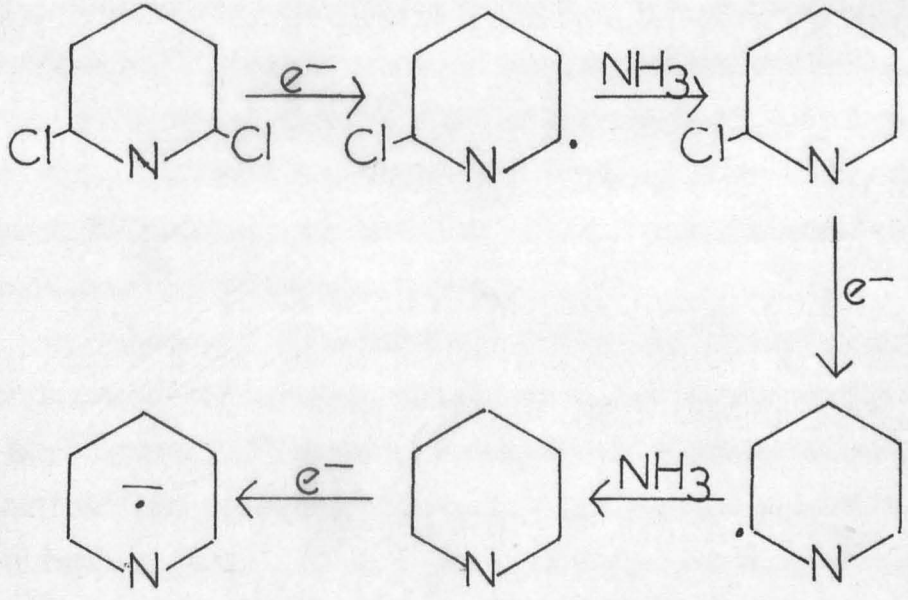
The mode of interaction between e^-_{solv} and methyl[38] and benzyl[128] chlorides and iodobenzene[111] has been shown by pulse radiolysis and matrix isolation to be one of dissociative electron attachment

$$RX + e^- \rightarrow R^\cdot + X^-$$

provided that the electron affinity of X exceeds the bond dissociation-energy of RX.

4.4.1. Chloro-, bromo-, and iodo-substituted compounds

With the exception of the fluoro-derivatives, for all the compounds listed in Table 4.1 the observed spectra can be rationalised in terms of an initial fast ($k_2 \geq 10^9$ l.mole^{-1} sec.$^{-1}$) production of an aryl radical which then undergoes rapid secondary reactions, involving an attack on the solvent or solute. Radicals from all the monosubstituted aromatics except iodobenzene appear to abstract hydrogen from either the solvent or cosolvent. The hydrocarbon so produced attaches a second electron to give the observed radical-anion. The polyhalogenated aromatics undergo a sequence of such steps, for example, for 2,6-dichloropyridine.

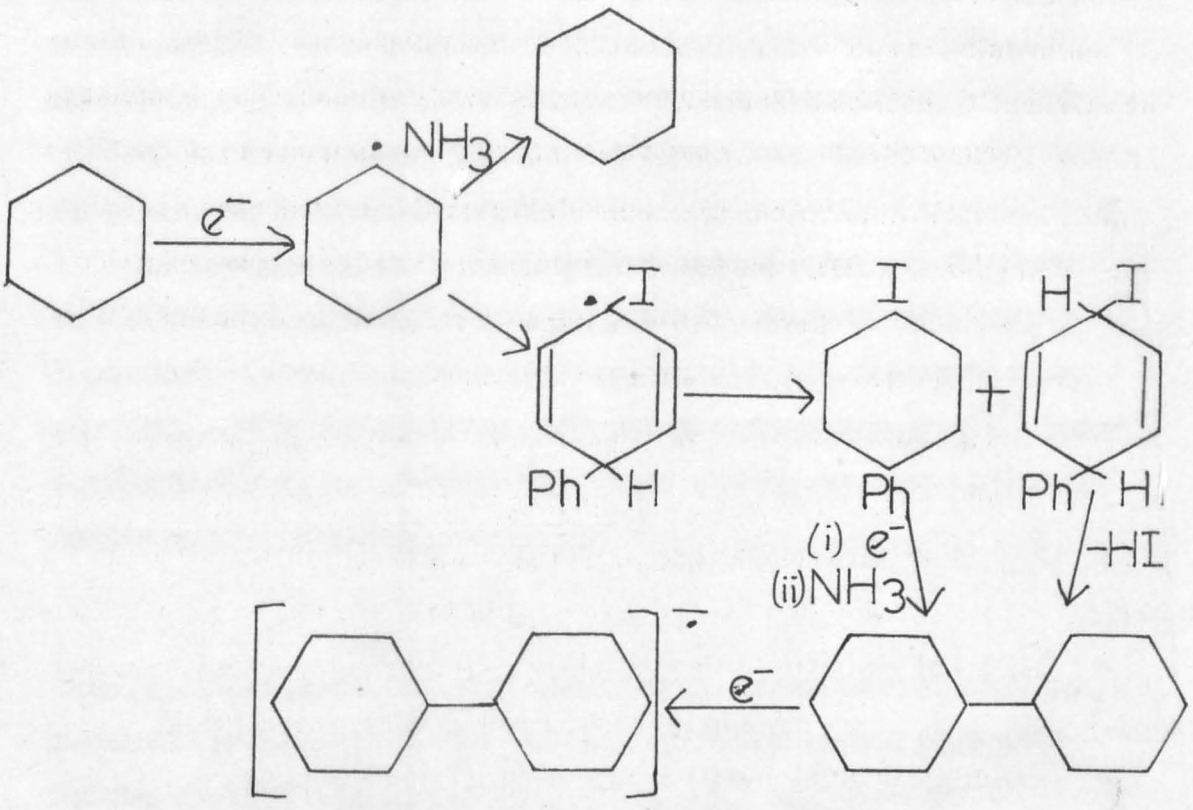


Electrolytic reduction[129] in dimethyl sulphoxide of some chloro-substituted nitropyridines and nitropyrimidines show the stepwise reduction mechanism. Reduction of 2-chloro-5-nitropyridine at about -0.9 v. gave

an e.s.r. spectrum exhibiting splitting due to the chlorine atom. Reduction of the same solution at -1.45 v. gave an e.s.r. spectrum identical with that of the 3-nitropyridine radical-anion, as did electrolysis of 2-chloro-3-nitropyridine. Electrolysis of 2-chloro-5-nitropyrimidine gave an initial unstable radical followed by a stable radical assigned to the 5-nitropyrimidine. These results further demonstrate the loss of chloride ion followed by abstraction of hydrogen and further electron addition.

In the cases of iodobenzene and 4-diiodobenzene, radical coupling or, more probably, attack of aryl radical upon substrate are important (but by no means exclusive)[101] and both compounds produce the well-known spectrum of the biphenyl radical-anion. The first stage of the reduction of iodobenzene has been characterised by means of the rotating cryostat technique,[111] and by photolysis in liquid solution.[107, 130] In each case the phenyl radical is the reactive intermediate, arising in the former case by dissociative electron attachment, and in the latter by dissociation. In benzene solution[107] the phenyl radical attacks a molecule of solvent to give biphenyl. It has been proposed[84] that in ammonia a carbanion is formed by the overall addition of two electrons to the phenyl halide to give ultimately benzene in 75% yield which is resistant to further attack by metal-ammonia solution alone[131] at low temperature.

The appearance of the relatively low intensity biphenyl radical-anion spectrum and the high concentration of benzene can be accounted for by the following mechanism. The phenyl radical formed in the initial reduction step can abstract hydrogen from the ammonia to give benzene which is inert to further reaction. Attack by the phenyl radical upon a further molecule of phenyl iodide can also occur, with subsequent reactions giving ultimately the stable biphenyl radical-anion.



It is not clear why reduction of bromobenzene, 2-diiodobenzene and 4-chloroiodobenzene gave no detectable signal, as presumably the reaction mechanism should apply also to these compounds.

According to the mechanism depicted, reduction of 3- and 4-iodotoluene should give bitolyl radical-anions. If these are unsymmetrical their e.s.r. spectra would be expected to be composed of small splittings from non-equivalent protons, and so be ill-resolved. Comparison between the spectra obtained and those of 4,4'-bitolyl[132] and 2,2'-bitolyl[133] negative ions show no similarities in either case, indicating the formation of unsymmetrical bitolyls.

4.4.2. Fluoro-substituted compounds

Fluoro-substituted pyridine and biphenyl behave quite differently from

halogeno-compounds discussed above. On a short time-scale both the fluoro-substituted compounds retain the fluorine atom to give the corresponding substituted radical-anion. Assignment of the experimental coupling constants to particular ring positions was made by comparison with the unsubstituted compounds and with MO calculations.

Comparison of the 2-fluoropyridine radical-anion with the parent radical-anion suggests splitting of the order of 4 oersted at the 2- and 6-positions, 1 oersted at the 3- and 5-positions and ca. 9 oersted at the 4-position. MO calculations using the values of Carrington et al[115] show a redistribution of charge around the ring due to the perturbing influence of the fluorine. Using the relationship[115]

$$a_F = Q^F \rho_C$$

where ρ_C is the pi-electron spin density on the carbon atom to which the fluorine is bonded and $Q^F = 50 \pm 10$ oe., the Hückel method predicts the fluorine splitting to be ca. $1.3 \times a_6$ with $a_6 \approx 4.3$ oe., while the McLachlan method suggests $a_F \approx a_6$ with $a_6 \approx 4.5$ oe. Values of ca. 8 oe. and 10 oe. are predicted by the Hückel and McLachlan methods respectively, for a_4. Both methods show ambiguity with the 3- and 5-positions, although it is likely that $a_3 > a_5$. In view of the fact that the value of a_F is usually about twice that of the corresponding a_H in the unsubstituted compound, for example, in the fluoronitrobenzenes,[115] and that Hückel spin densities show better agreement with experiment, the assignment shown in Table 4.1 is based largely on the Hückel values.

MO calculations on the 2,2'-difluorobiphenyl system, using the parameter values[115] $k_{C-F} = 0.7$, $h_F = 1.6$, and $\delta_C = 0.1$ (auxiliary inductive parameter for the carbon atom bonded to fluorine, defined by $\alpha_C = \alpha_O + \delta h_F \beta_O$), and $k_{C-F} = 0.7$, $h_F = 3.0$, and $\delta_C = 0.1$[118] gave almost identical results, the McLachlan treatment giving better general agreement with experiment. The assignment shown in Table 4.1 is based on

the McLachlan spin densities.

The behaviour of the fluoro-substituted compounds towards reduction can be explained in terms of the relatively greater bond energy for a carbon-fluorine bond than for a bond between carbon and the other halogens. Allred and Bush[118] attribute the stability of the C-F bond in part also to the lack of transfer of the unpaired electron to the fluorine atom, whereas occupation of vacant d-orbitals in the other halogens can occur, resulting in the immediate formation of halide ions. The C-F bond in 2-fluoropyridine is sufficiently strong to withstand the extra electron density associated with the radical-anion, but loss of fluoride ion occurs with the fluorobiphenyl, though more slowly than the other halogens. Subsequent hydrogen abstraction and electron addition gives ultimately the biphenyl radical-anion.

4.4.3. Halobenzonitriles

In Table 4.2. are given the coupling constants of the three monofluoro-substituted benzonitriles. The assignments indicated therein are based on MO calculations and on comparison with the unsubstituted species. Calculations on benzonitrile were first performed to obtain the empirical parameters for the nitrile group. A number of values were tried, but as Rieger and Fraenkel reported,[134] no reasonable choice of parameters would produce both the correct magnitude of the splittings and the correct ortho to para ratio. Their suggested values of $k_{C'-C} = 0.9$, $k_{C\equiv N} = 2.0$, $h_N = 1.0$ were used throughout as these gave the best overall fit with experiment, though both the Hückel and McLachlan treatments underestimated the magnitude of the spin densities of the 2- and 4-positions. Consequently, the theoretical spin densities in the fluorobenzonitriles are lacking in accuracy, although they show qualitative trends which can be used for assignment purposes. The fluorine parameters giving best overall fit with experiment are $k_{C-F} = 0.7$, $h_F = 3.0$ and $\delta_C = 0.1$. The spin densities so obtained are given in Table 4.2. Generally the McLachlan procedure gives values closer to the experimental values and

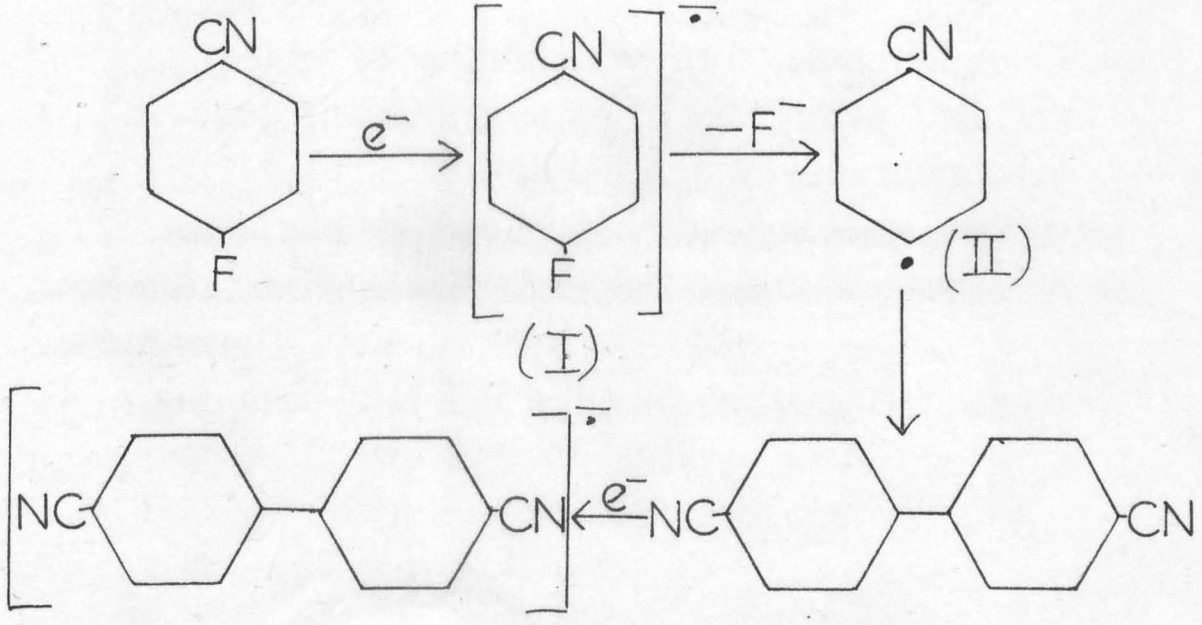
the assignments are based on the spin densities derived by this method.

A value of $\left|Q_{CH}^{H}\right|$ = 23.6 oersted was used to correlate proton coupling constants with spin densities throughout. The most general equation correlating fluorine coupling constants with spin densities is an adaptation of the Karplus-Fraenkel equation (Chapter 1, equation (7)), with suitable choice of sigma-pi parameter values. However, there is some discrepancy in the choice of these values[135] and it was suggested that the equation[115]

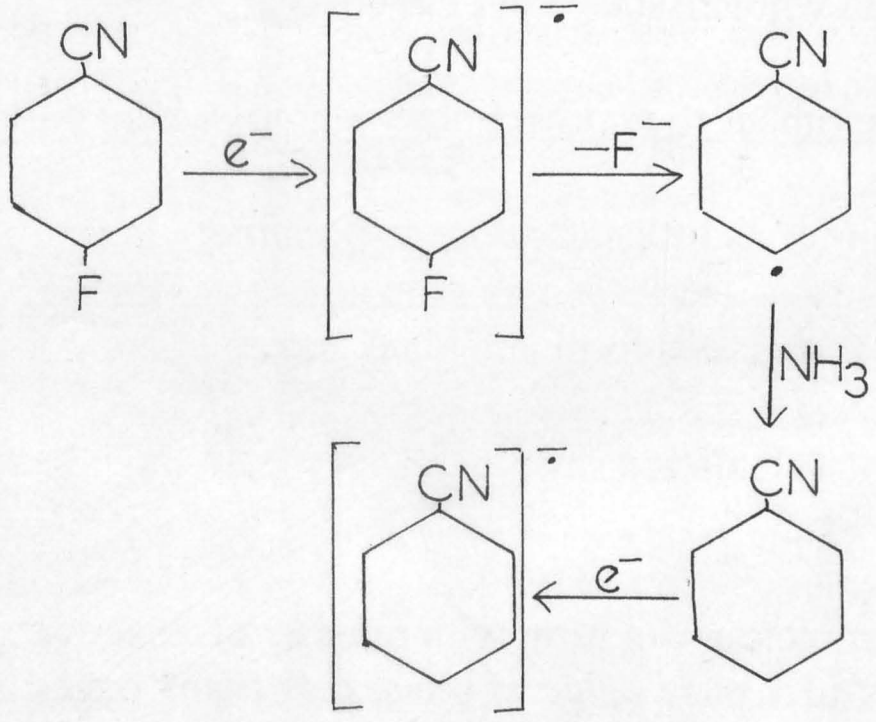
$$a_F = Q^F \rho_C$$

with $Q^F = 50 \pm 10$ oe. gave equally good correlation as the more general equation, and this equation was used in the present calculations.

Ring substitution by electronegative groups greatly modifies the tendency of aryl halides to shed halogen on reduction; for example, some monohalogeno-substituted nitrobenzenes readily lose halogen on electrolysis, and others less readily or not at all.[136] The electrolytic reduction of 4-fluorobenzonitrile in N,N-dimethylformamide produces the radical-anion of 4,4'-dicyanobiphenyl,[125] indicating that the presence of a cyano-group on fluorobenzene labilises the carbon-fluorine bond. This suggests the reaction sequence :



It is clear that for all three fluoro-substituted benzonitriles the first stage of the reduction is the formation of a radical-anion such as (I). The 2- and 4-substituted compounds then give the aryl radical (II), the rate of loss of fluoride ion being greatest in the 4-substituted case. In DMF, radical dimerisation occurs, followed by a one-electron addition to give the 4,4'-dicyanobiphenyl radical-anion, while in ammonia hydrogen abstraction occurs in a similar manner to the halogeno-compounds discussed above; for example with 4-fluorobenzonitrile.



Loss of halide ion from the chlorobenzonitriles occurs on a shorter time-scale, the only paramagnetic species observed being the benzonitrile radical-anion.

CHAPTER 5

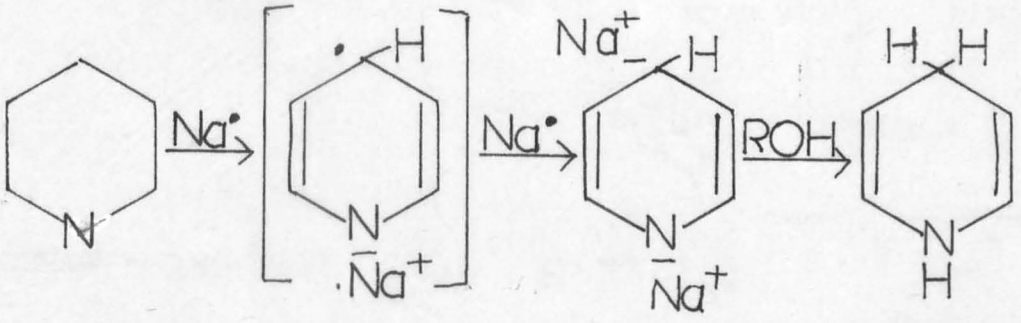
REDUCTION OF NITROGEN HETEROCYCLICS

5.1. INTRODUCTION

Substitution of an electronegative group into an aromatic ring greatly facilitates reduction ; for example, pyridine is much more readily reduced than benzene because the electronegative heteroatom is better able than carbon to stabilise the resulting negative charge. Depending on the method and conditions of the reduction of pyridine, two possible main types of products arise (i) ring-hydrogenated pyridines, and (ii) bipyridyls.

Partial or total hydrogenation of pyridine occurs in the presence of a proton source in the reaction medium, or by catalytic reduction. Sodium in ethanol reduces pyridine to 1,4-dihydropyridine[137] while in butanol[138] a tetrahydropyridine is formed. Reduction of some 2-alkyl pyridines with sodium and alcohol in liquid ammonia gives the corresponding 1,4-dihydro-derivatives.[139] Electrochemical[140] and catalytic[141] reductions of pyridine and its homologues give the corresponding piperidines.

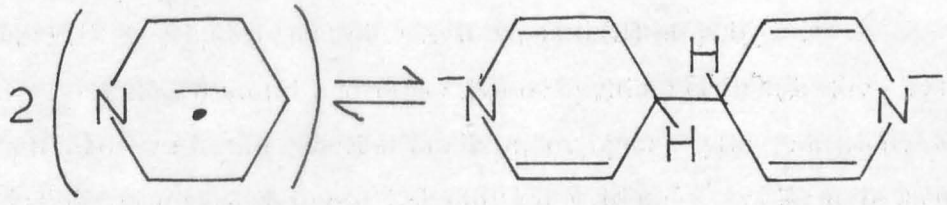
The formation of the dihydropyridines can be represented by :



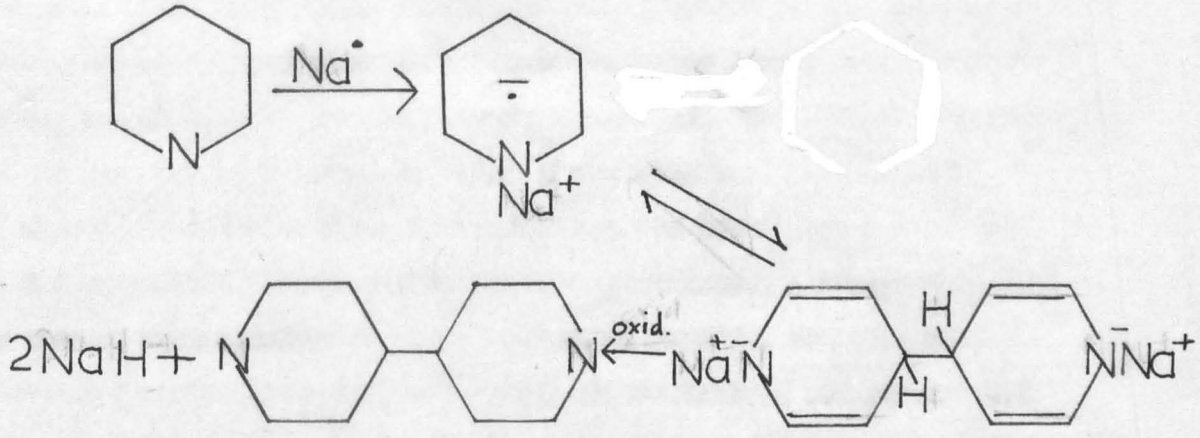
Further reduction is supposed to occur by similar steps.

Unlike simple aromatic hydrocarbons, the alkali metal reduction of

pyridine in ethereal solution,[142] liquid ammonia alone,[143] hexamethylphosphoramide (HMPA),[144] or neat pyridine[145, 146] does not terminate at the simple radical-anion stage, but instead a dimerisation takes place yielding as the end-product 4,4'-bipyridyl. It is found that reduction by sodium in HMPA solution[144] produces an equilibrium quantity (ca. 10^{-5}M) of the monomer radical-anion by virtue of the reaction :



Excess of sodium effects aromatisation of the diamagnetic dianion to give bipyridyl and sodium hydride. In neat pyridine the aromatisation proceeds in the absence of excess sodium.[146] These results can be explained in terms of the reactions :



In none of these cases is any hydrogenated pyridine or hydrogenated bipyridyl produced.

Optical[147] and e.s.r.[142, 148] spectroscopic techniques have been

used to observe the path of this reductive dimerisation reaction, but the initial intermediate, the pyridine radical-anion, proved to be too unstable for detection, the 4,4'-bipyridyl radical-anion only being observed. This prompted us to apply the fast-mixing device and flow-system described above to enable observation by e.s.r. of the monomer radical-anions of pyridine and some methyl-, methoxy-, and carboxy-substituted pyridines. Since beginning this work, reports have appeared of the production of the pyridine radical-anion[66, 144] and some of its methyl derivatives.[66] The e.s.r. spectra of the relatively stable radical-anions of 3,5-dimethylpyridine,[149] 4-cyanopyridine,[126, 150] tetra- and penta-cyanopyridines,[151] 3-[152] and 4-[153] nitropyridines, 4-acetylpyridine[63] and methyl- and ethyl-nicotinates[154] have been presented. A number of other stable nitrogen heterocyclics have been studied, and their e.s.r. spectra obtained, including acridine and many azines.[19, 148, 155]

The present work was undertaken in an attempt to study the reduction of pyridine and a number of its derivatives by dilute solutions of sodium in liquid ammonia. Observation is made within a few milliseconds of the formation of the radicals and continuous renewal of the sample reduces or eliminates the effect of secondary reactions, unless longer delays between mixing and observation are deliberately introduced. The further course of the reaction can be observed by e.s.r. if any additional paramagnetic intermediates or stable products are formed, and this has been achieved by making observations up to a few minutes after mixing. Analyses of the spectra were obtained in every case where possible, and assignment of coupling constants to particular ring positions made by comparison with MO spin density calculations, using the relations between coupling constants and spin densities given in Chapter 1.

5.2. EXPERIMENTAL

Concentrations of 2×10^{-3} M substrate and 5×10^{-3} M sodium in ammonia were generally used, allowing optimum signal size and resolution in most cases. Some compounds required a rather high modulation amplitude to give satisfactory signal size and consequently this led to a lowering of resolution. Pyridine-2,3- and -2,4- dicarboxylic acids are not soluble to the extent of 2×10^{-3} M in ammonia alone, and 200 ml. of purified tetrahydrofuran were used as cosolvent, although the spectra obtained in the mixed solvent were no better than those from the saturated solutions in ammonia alone. Maximum flow rates were used initially in each experiment, but no changes in any of the spectra were apparent on using lower flow rates.

Static experiments were conducted as described in Chapter 3. Initially the strong electron signal was present but stirring caused its immediate disappearance. In this way spectra could be obtained within 1 - 2 minutes of sample preparation, and in some cases decay of the first paramagnetic species and build-up of the dimer species could be easily followed.

Reduction of pyridine in the presence of ethanol was carried out by adding to a solution of pyridine in ammonia the required amount of ethanol. The reductant solution was made up as normal. The two solutions were then mixed as described previously.

Materials

All the materials, with the exception of pyridine-2,6-dicarboxylic acid diethyl ester and the corresponding N-oxide were commercial products and were purified by distillation or recrystallisation where necessary. Reduction of 2,4,6-trimethylpyridine (B.D.H. product) gave an e.s.r. spectrum identical to that of the 3,5-dimethylpyridine radical-anion. Attempted analysis of this material by G.L.C. was made but no separation of the trimethyl- and dimethylpyridine peaks could be achieved, so the purity of the trimethylpyridine could

not be determined. Proton n.m.r. spectra of the two compounds were taken, the two spectra being dissimilar, but again no estimate of the purity could be made. 2,4,6-trimethylpyridine (Hopkin and Williams, Material for Chromatography grade) was examined, the e.s.r. spectrum obtained on its reduction showing the presence of two species. The material purchased from Reilly Tar Co. (assay 97% trimethylpyridine, guaranteed free of 3,5-dimethylpyridine) failed to give a signal on reduction, although the blue colour of the solvated electron was destroyed, indicating that reaction had occurred.

Pyridine-2,6-dicarboxylic acid diethyl ester (diethyl dipicolinate)

The diester was prepared from the acid by the method of Barnes and Fales.[156] Yield, using same quantities, 10.4 gm. M.Pt. 40 - 42° (Lit. 41 - 42°).

Pyridine-2,6-dicarboxylic acid-N-oxide

The N-oxide was prepared from the acid by the method of Heywood and Dunn.[157] Yield, using same quantities, 2.0 gm. Decomp. 163°. (Lit. M.Pt. 155 - 157° : Catalogue decomp. 163°).

5.3. RESULTS AND ANALYSIS OF SPECTRA

The coupling constants for the nitrogen heterocyclic radicals are given in Table 5.1.

5.3.1. Pyridine, pyridine-N-oxide, and pyrimidine

Flow experiments

The first spectrum obtained was that from the reduction of pyridine itself. The spectrum is analysed in terms of a 1 :1 :1 triplet, two unequal 1 :2 :1 triplets and a 1 :1 doublet. This splitting pattern can only arise by interaction of the unpaired electron with a single nitrogen nucleus, two groups of two equivalent protons and a single proton and so must be assigned to the

TABLE 5.1.

COUPLING CONSTANTS OF RADICAL-ANIONS PRODUCED FROM PYRIDINE AND DERIVATIVES[a]

Substrate	Coupling Constants (oersted) N	2	3	4	5	6	g-value
Pyridine	6.31	3.55[c]	0.79[d]	9.63			2.0034
Pyridine dimer[b]	4.08	0.56[c]	2.70[d]				
Pentadeuteropyridine	6.38	0.50[c]	0.13[d]	1.49			2.0035
Pentadeuteropyridine dimer[b]	3.59	0.07[c]	0.36[d]				
Pyridine-N-oxide	11.00	3.03[c]	0.43[d]	8.52			2.0035
Pyrimidine	3.28[e]	0.75		9.80[f]	1.33		2.0025
4,4'-Bipyrimidine	3.14	1.57	1.57		1.57	0.20	
2-Methylpyridine	5.64	2.34[g]	1.56	9.53	<0.1	4.39	2.0034
2-Methylpyridine dimer[b]	2.75	0.60[g]	2.75		1.82	0.18	
3-Methylpyridine	6.34	4.07	0.45[g]	9.61	1.35	2.68	2.0036
3-Methylpyridine dimer[b]	3.57	2.08	1.93[g]		2.39	0.45	
4-Methylpyridine	5.67	3.68[c]	0,058[d]	11.31[g]			2.0033
2,3-Dimethylpyridine	5.78	2.89[g]	0.46[g]	8.66	0.82	2.89	2.0034
2,6-Dimethylpyridine	4.86	3.16[c,g]	0.71[d]	9.29			2.0033
2,6-Dimethylpyridine dimer[b]	3.11	0.27[c,g]	2.36[d]				
3,4-Dimethylpyridine	5.77	4.98	<0.2	11.48[g]	1.51	2.34	2.0033
3,5-Dimethylpyridine	6.40	3.18[c]	1.06[d,g]	8.85			2.0034
3,5-Dimethylpyridine dimer[b]	3.71	0.58[c]	1.85[d,g]				

....continued

TABLE 5.1. (continued)

Substrate	N	Coupling Constants (oersted) 2	3	4	5	6	g-value
2-Methoxypyridine	8.86	0.23[h]	1.09	7.14	0.46	4.29	2.0032
2,6-Dimethoxypyridine	4.41	≈0.15[c,h]	0.83[d]	10.16			2.0032
2,6-Dimethoxypyridine dimer[b]	2.68	0.14[c,h]	2.56[d]				

a Assignments based on MO calculations ;

b 'dimer' refers to the corresponding 4,4'-bipyridyl ;

c $a_2 = a_6$;

d $a_3 = a_5$;

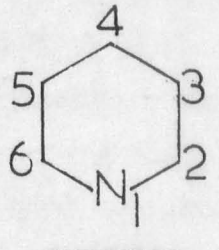
e $a_1 = a_3$;

f $a_4 = a_6$;

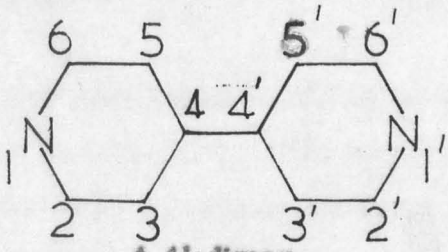
g methyl proton coupling constant ;

h methoxy proton coupling constant.

The compounds in the table are labelled as :



monomer



4,4'-dimer

pyridine radical-anion itself rather than the dimer. The coupling constants are in good agreement with those of Talcott and Myers[66] but differ somewhat from those of Chaudhuri et al.,[144] who carried out the reduction of pyridine in HMPA. The spectrum obtained by the reduction of pentadeuteropyridine is entirely consistent with this interpretation, the splitting patterns for each group changing as expected, and the deuterium splittings being related to the corresponding proton splittings by a factor of $a_D/a_H \approx 0.15$, as would be expected if the deuterium atoms were in a magnetic environment similar to the protons. The spectrum of $C_5D_5N^{\cdot -}$ is shown in Figure 5.1.

Flow reduction of pyridine-N-oxide gave a very well resolved spectrum assigned to the N-oxide radical-anion. The coupling constants are in excellent agreement with those of Talcott and Myers.[66] The spectrum was unchanged on observation 1.0 sec. after mixing.

Pyrimidine produced a well resolved spectrum on reduction exhibiting splittings from two equivalent nitrogen atoms, two equivalent protons and two non-equivalent protons. This is the expected pattern from the monomer radical-anion and the spectrum is assigned to this species, again in agreement with Talcott and Myers.[66]

Static experiments

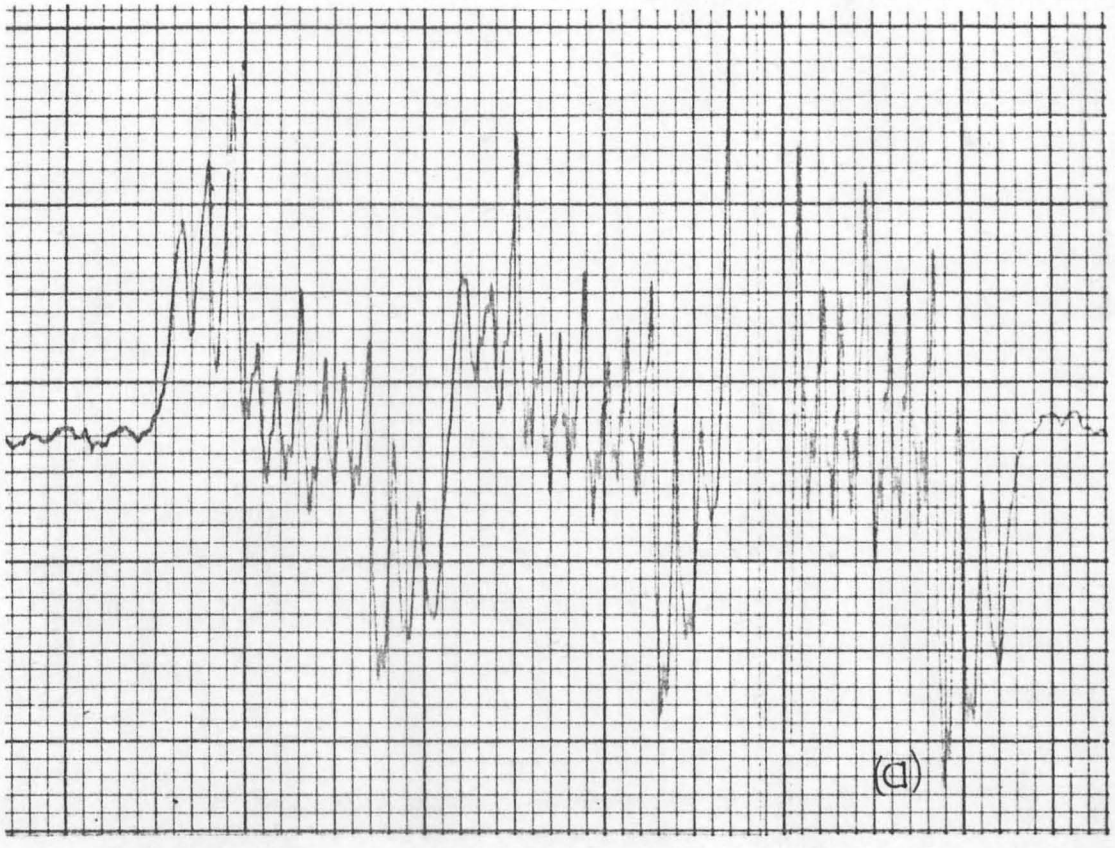
Pyridine itself produced only the 4,4'-bipyridyl radical-anion even within 1 min. of mixing. The coupling constants are in good agreement with those obtained by reduction of pyridine in ethereal solvents.[142] Little decay of the signal was apparent after 1 hour. Pentadeuteropyridine gave only the 4,4'-dimer radical-anion, although the resolution of the spectrum improved over a longer time interval. The ratio of the deuterium to the proton coupling constants is again ca. 0.15.

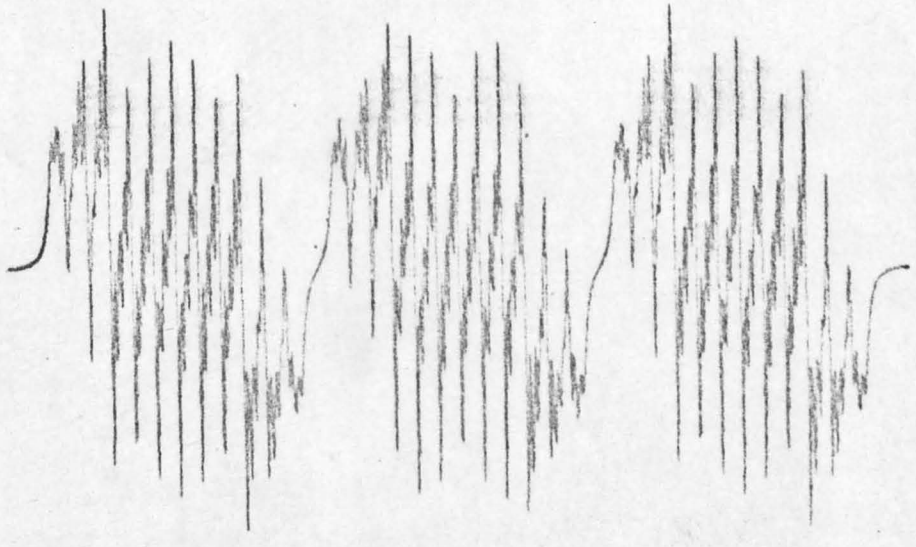
Reduction of pyridine-N-oxide gave initially a poorly resolved spectrum, very similar to that of the pyridine radical-anion. This decayed slowly over a period of 20 mins. and simultaneously a more complex signal appeared until

FIGURE 5.1.

(a) Spectrum from pentadeuteropyridine

(b) Computer simulated spectrum


(a)


(b)

after ca. 40 mins., only this signal remained. Inspection of this spectrum showed it to be identical to that produced on reduction of 2,2'-bipyridyl, and so it is assigned to the 2,2'-bipyridyl radical-anion. The coupling constants $a_{2N} = 0.80$, $a_{2H} = 0.22$, $a_{2H} = 2.47$, and $a_{4H} = 4.94$ oe. produce excellent agreement with the experimental spectrum on computer simulation, although they are in contrast to the values obtained in ethereal solvents.[158] No pyridine-N-oxide radical-anion was detected.

Pyrimidine gave a well resolved spectrum composed of 17 lines, each being a 1 :2 :1 triplet. The spectrum was stable for over an hour and was the only species observed, no monomer radical-anion being detected.

Equally good simulation of the experimental spectrum was found with two sets of coupling constants, each set suggesting the formation of a dimer, but with the bond between different atoms. The set of coupling constants $a_{4N} = 1.60$, $a_{4H} = 3.17$, and $a_{2H} = 0.20$ oe. suggest the formation of a symmetrical dimer, while the set $a_{2H} = 0.20$, $a_{4H} = 1.57$, $a_{2N} = 1.57$, and $a_{2N} = 3.14$ oe. indicates formation of a dimer in which the four nitrogen atoms are not equivalent. A discussion of the choice of coupling constants is given in Section 5.4.3. below.

5.3.2. Alkyl-substituted pyridines

Flow experiments

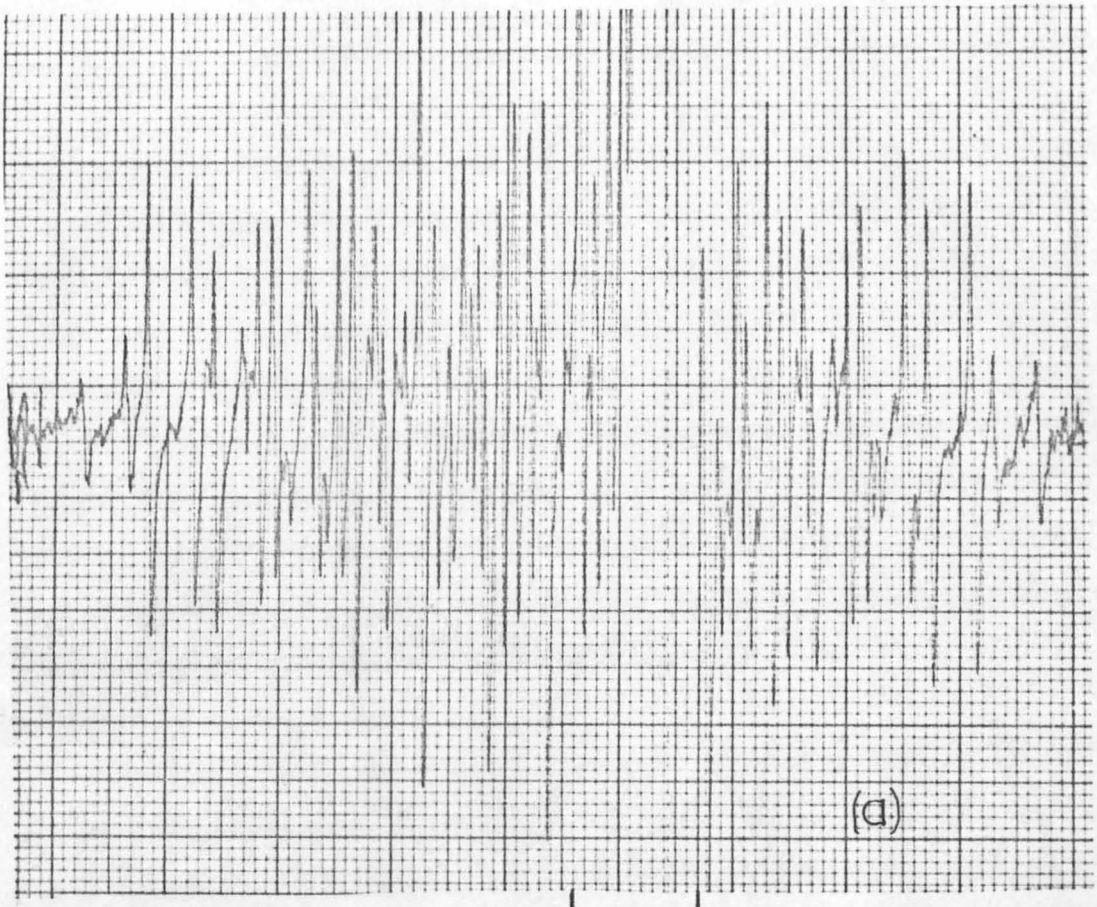
The spectra obtained on the flow reduction of the three monomethyl-pyridines (picolines) can all be interpreted in terms of the monomer radical-anion. The spectrum of the 2-picoline radical-anion is shown in Figure 5.2. The coupling constants of the 4-picoline radical-anion are in good agreement with those obtained by Talcott and Myers.[66]

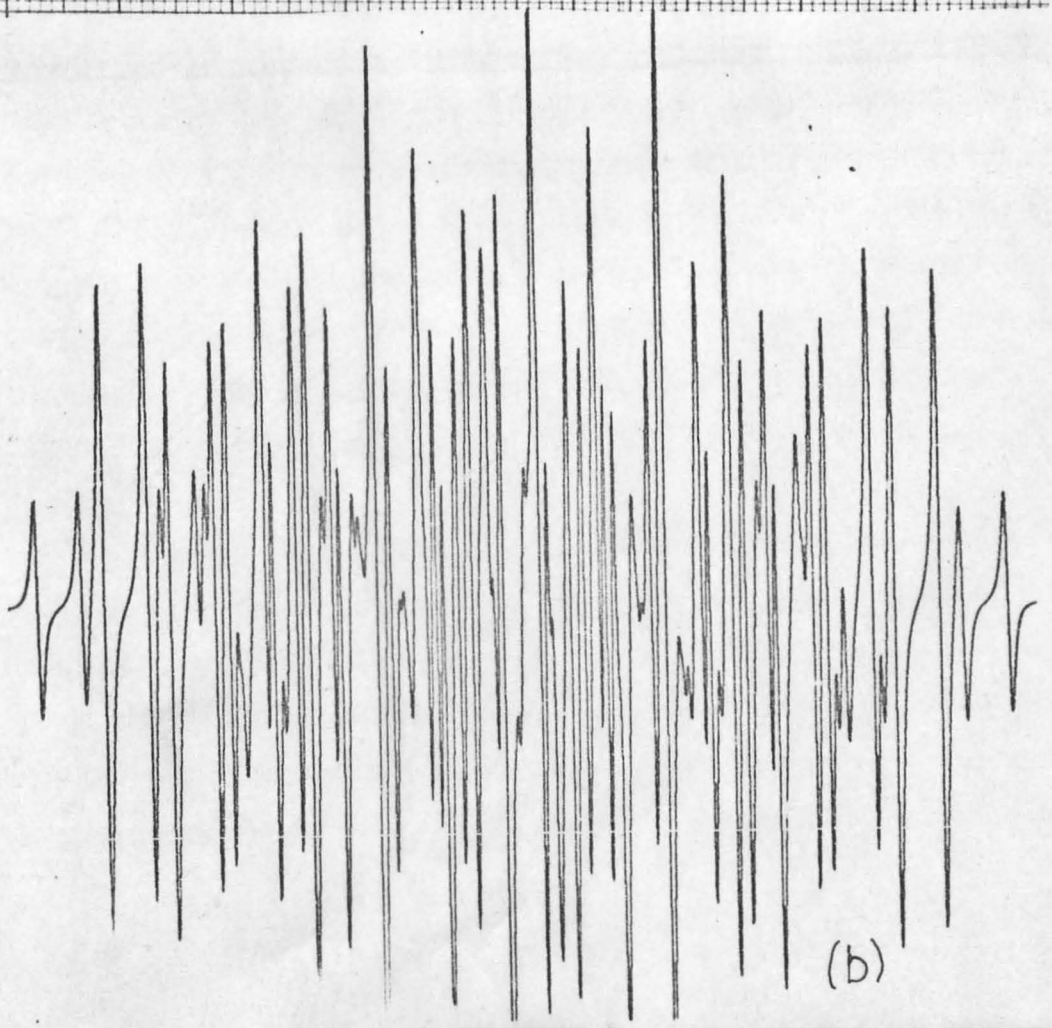
2,3-, 2,6-, 3,4-, and 3,5-Dimethylpyridines (lutidines) all gave e.s.r. spectra on reduction which are interpreted in terms of monomer radical-anions. Due to the large number of lines expected, particularly from the

FIGURE 5.2.

(a) Spectrum from 2-methylpyridine

(b) Computer simulated spectrum


(a)


(b)

unsymmetrical lutidines, and line widths of the order of 0.2 oe., a large amount of overlap occurs, making analysis sometimes difficult. In these cases, analysis is taken as being correct only if a good fit between simulated and experimental line positions and intensities is obtained, stick-diagrams being more open to doubt.

2,3,6-Trimethylpyridine (2,3,6-collidine) gave a low intensity spectrum composed of broad lines which could not be interpreted. As mentioned in Section 5.2, the spectrum from 2,4,6-collidine is marred by the presence of 3,5-lutidine. The MFC grade collidine gave a small signal other than that due to 3,5-lutidine, but no analysis could be made.

Static experiments

Static reduction of 2-picoline gave a spectrum identical to that of the monomer radical-anion, though less well resolved, which decayed (half-life ca. 5 mins.) and was replaced by a more complex spectrum. Analysis proved difficult but the coupling constants expected for a 4,4'-dimer species, and shown in Table 5.1, reproduce the experimental spectrum very well. 3-Picoline immediately gave a spectrum which was stable over a period of hours, and was unlike the monomer species. Again, analysis was difficult, but the coupling constants of Table 5.1, based on 4,4'-dimer formation, reproduce the experimental spectrum fairly well. 4-Picoline exhibited the spectrum of the monomer radical-anion which rapidly decayed (half-life ca. 1 min.) to diamagnetic products. No further signal was obtained within an hour of mixing.

Nine broad lines, similar in their coarse features to the monomer species, were obtained on static reduction of 2,3-lutidine. Decay of this signal occurred after a few minutes to give a multiline spectrum, dissimilar to the monomer, but no analysis could be made. A superposition of two spectra was obtained with 2,6-lutidine, one decaying while the other grew to give a species stable for ca. 30 mins. The spectrum of the more stable

species is analysed in terms of splitting from two equivalent nitrogen atoms, four equivalent protons and twelve equivalent protons, which can only arise from the 4,4'-dimer. The spectrum is shown in Figure 5.3. 3,4-Lutidine gave a small signal which rapidly decayed to diamagnetic products. Initially a spectrum identical to the monomer radical-anion signal was present with 3,5-lutidine. This decayed with a half-life of ca. 4 mins. and after 3 mins. a second species appeared which then remained for about 45 mins. Splitting from two equivalent nitrogen atoms, four equivalent protons and twelve equivalent protons is apparent, indicating the presence of the 4,4'-dimer. The observation of the decay of the monomer species is in accord with the observation of Talcott and Myers[66] but contrasts with that of Atherton et al.[149] who record no dimerisation in 1,2-dimethoxyethane on reduction with a potassium film.

2,3,6-Collidine gave a wide (41 oe.) multiline spectrum which, though well resolved, has not yet been analysed. None of the 2,4,6-collidine samples gave a signal on static reduction although the discharge of the blue colour of the solvated electron indicated rapid reaction.

5.3.3. Methoxy- and hydroxy-substituted pyridines

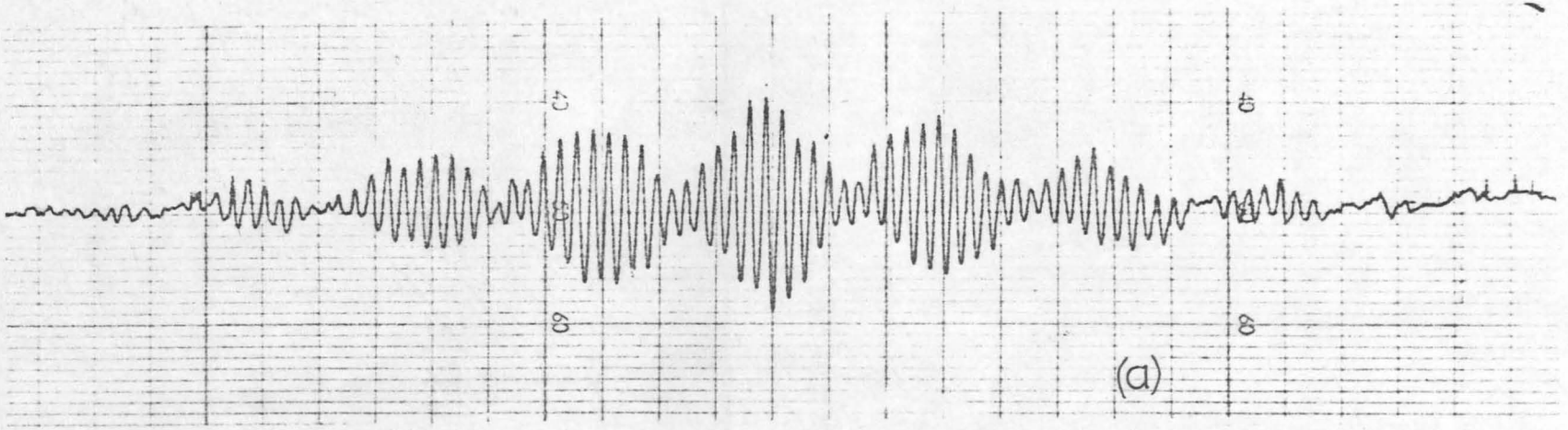
Flow experiments

A number of runs with 2-methoxypyridine as substrate produced spectra from which all coupling constants could be obtained. Substrate at 2×10^{-3} M and sodium at 5×10^{-3} M gave spectra showing little resolution of the methoxy proton hyperfine structure, but sodium at ca. 10^{-3} M allowed resolution of this splitting despite the low signal intensity. Measurements from a number of spectra gave all the coupling constants. Similar treatment of 2,6-dimethoxypyridine allowed measurement of the methoxy proton coupling constant. Alternatively, a high substrate flow-rate combined with a low reductant flow-rate produced small spectra with excellent resolution.

FIGURE 5.3.

(a) Spectrum from 2,6-dimethylpyridine dimer

(b) Computer simulated spectrum



(a)

(b)

Analysis indicates formation of the monomer radical-anions.

Reduction of 3- and 4-hydroxypyridines gave no signal in either case although the blue colour of the reductant solution disappeared immediately on mixing, indicating a fast reaction.

Static experiments

Static reduction of 2-methoxypyridine gave initially the 2-methoxypyridine radical-anion spectrum which was rapidly superseded by a more complex signal, which, though it has not yet been analysed completely, is indicative of the 4,4'-dimer. 2,6-dimethoxypyridine showed only one spectrum which was stable for over an hour. Unambiguous analysis in terms of two equivalent nitrogen atoms, four equivalent protons and twelve equivalent protons accords with the 4,4'-dimer radical-anion.

No spectra were apparent on observation one minute after mixing with 3- or 4-hydroxypyridines.

5.3.4. Pyridine-ethanol, and mono- and di-carboxy substituted pyridines

Flow experiments

Reduction of pyridine in the presence of ethanol gave products dependent on the concentration of the ethanol. Pyridine and sodium concentrations were kept constant at 2×10^{-3} M and 5×10^{-3} M respectively, while the ethanol concentration was varied. For ethanol concentrations of 10^{-2} and 10^{-1} M, the e.s.r. spectrum obtained on reduction was identical to that of the pyridine radical-anion, while at ethanol concentrations greater than 1 M, a different species was present. The spectrum shows splittings from a single nitrogen nucleus, two unequal groups of two equivalent protons and two unequal single nuclei of spin 1/2, and is illustrated in Figure 5.4, the coupling constants being given in Table 5.2.

Two different spectra were obtained on reduction of pyridine-2-

TABLE 5.2.

COUPLING CONSTANTS FOR RADICALS PRODUCED FROM PYRIDINE-ETHANOL AND THE PYRIDINE CARBOXYLIC ACIDS [a]

	Coupling Constants (oersted)							g-value
	N	2	3	4	5	6	N-H	
Pyridine-ethanol	5.79	5.79[b]	0.74[c]	11.62			4.21	2.0038
Pyridine-2-carboxylic acid [d]	4.1			5.5			4.1	2.0036
Pyridine-3-carboxylic acid	1.64	1.09		7.28	0.47	8.83		2.0034
Pyridine-4-carboxylic acid	5.51	1.96	1.96					2.0037
Pyridine-2,3-dicarboxylic acid	0.85			3.41	3.41	0.85	0.85	2.0038
Pyridine-2,5-dicarboxylic acid	4.22		1.59	8.51		0.91	4.68	2.0036
Pyridine-2,6-dicarboxylic acid	6.16		0.83[c]	9.07			5.63	2.0035
Pyridine-2,6-dicarboxylic acid diethyl ester	3.08	0.60[b,e]	1.19[c]	9.93				2.0037
Pyridine-3,5-dicarboxylic acid	4.78	5.52[b]		12.31			3.86	2.0033
6-Methylpyridine-2,4-dicarboxylic acid	5.05		1.36		3.36	2.70[f]	4.03	2.0035

[a] Assignments based on MO calculations;

[b] $a_2 = a_6$;

[c] $a_3 = a_5$;

[d] assignment uncertain;

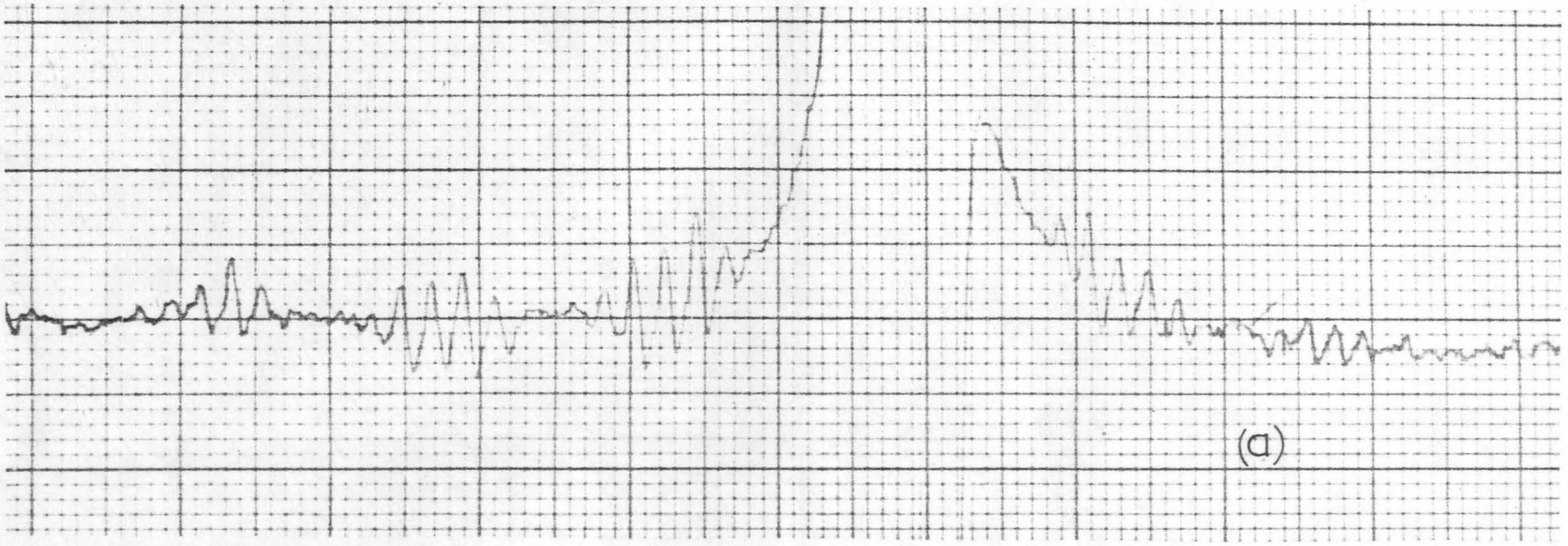
[e] ester proton coupling constant;

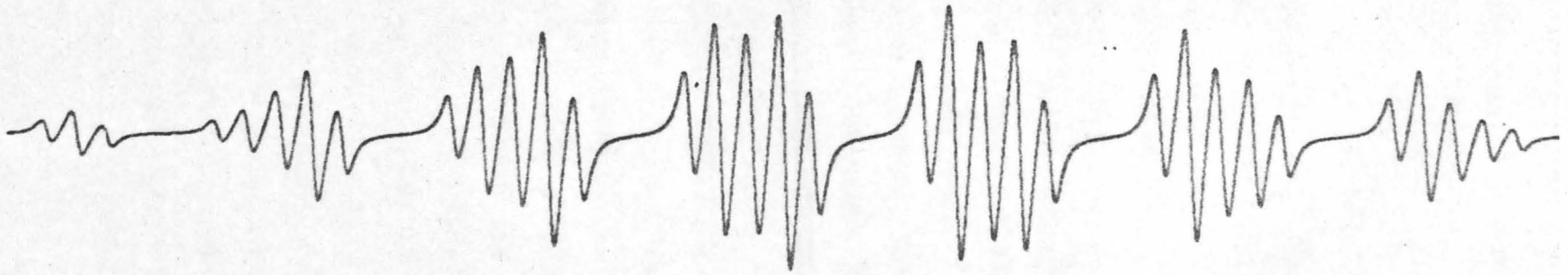
[f] methyl proton coupling constant.

FIGURE 5.4.

(a) Spectrum from protonated pyridine

(b) Computer simulated spectrum





(b)

carboxylic acid, the two species responsible being obtained under similar reaction conditions. One spectrum consists of eight lines and is analysed in terms of $a_N = a_H = 4.1$ oe. and $a_H = 5.5$ oe., and is obtained at 2×10^{-3}, 5×10^{-3} and 10^{-2} M concentrations. The line width is ca. 0.7 oe. The second spectrum, obtained only at a substrate concentration of 5×10^{-3} M, is more complex, wider and has a line width of 0.3 oe. Some lines in this spectrum have very low intensities compared to the outermost lines, and others cannot be accounted for using reasonable values for the coupling constants. These anomalies have so far prevented analysis of the spectrum and definite conclusions as to its origin cannot be made. Pyridine-3-carboxylic acid gave a spectrum showing splittings from a single nitrogen nucleus and four non-equivalent protons, while pyridine-4-carboxylic acid showed splittings from a single nitrogen nucleus and four equivalent protons. This is the expected behaviour as the carboxyl group possesses no magnetic nuclei in its ionised form. The spectrum from pyridine-4-carboxylic acid is shown in Figure 5.5.

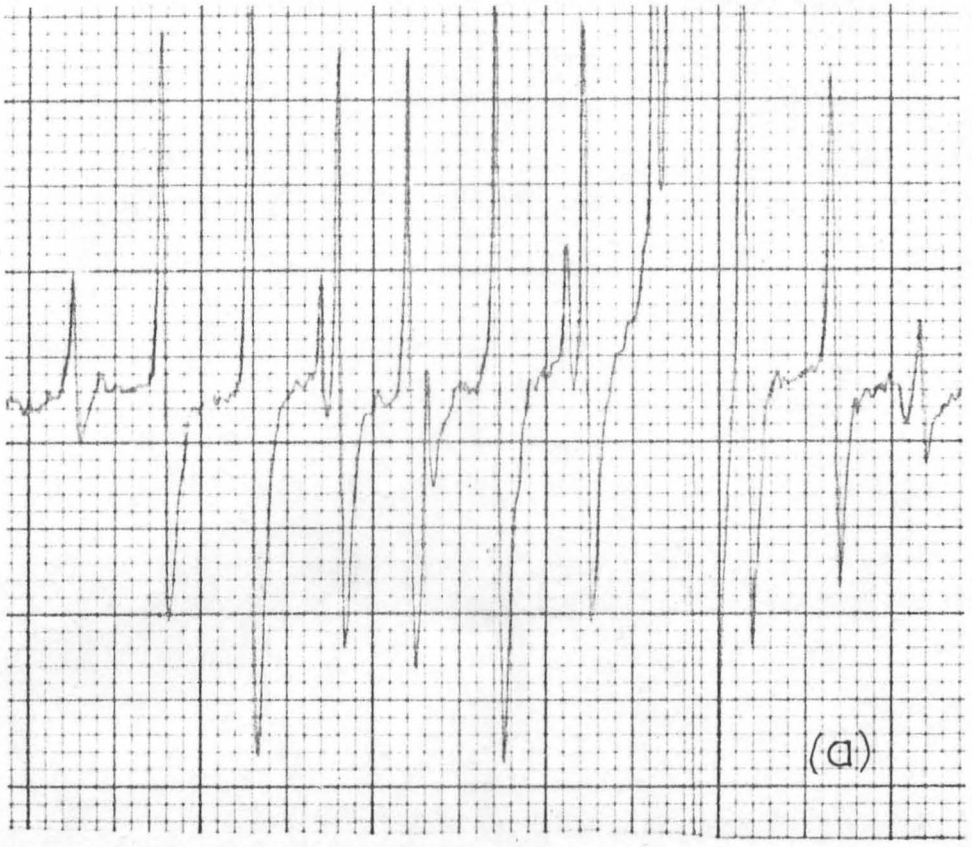
Excepting pyridine-2,4-dicarboxylic acid which gave a signal too small to analyse, the pyridine dicarboxylic acids all show one feature in common, namely, a doublet splitting extra to the number expected. Pyridine-2,3-, 2,5-, 2,6- and 3,5-dicarboxylic acids gave well resolved spectra with the coupling constants given in Table 5.2. The spectra obtained from the 2,6- and 3,5-dicarboxylic acids are shown in Figures 5.6 and 5.7 respectively. 6-Methyl-2,4-dicarboxypyridine gave a small but well resolved spectrum also showing an extra doublet splitting.

Reduction of 2,6-dicarboxypyridine at 5×10^{-3} M with sodium in ammonia in the presence of potassium amide at 10^{-2} M gave no signal other than the solvated electron line which was broader than normally obtained, although the eluate was yellow, indicating some reaction. Reduction of the N-oxide of this acid gave a well resolved spectrum identical to that obtained

FIGURE 5.5.

(a) Spectrum from pyridine-4-carboxylic acid

(b) Computer simulated spectrum


(a)

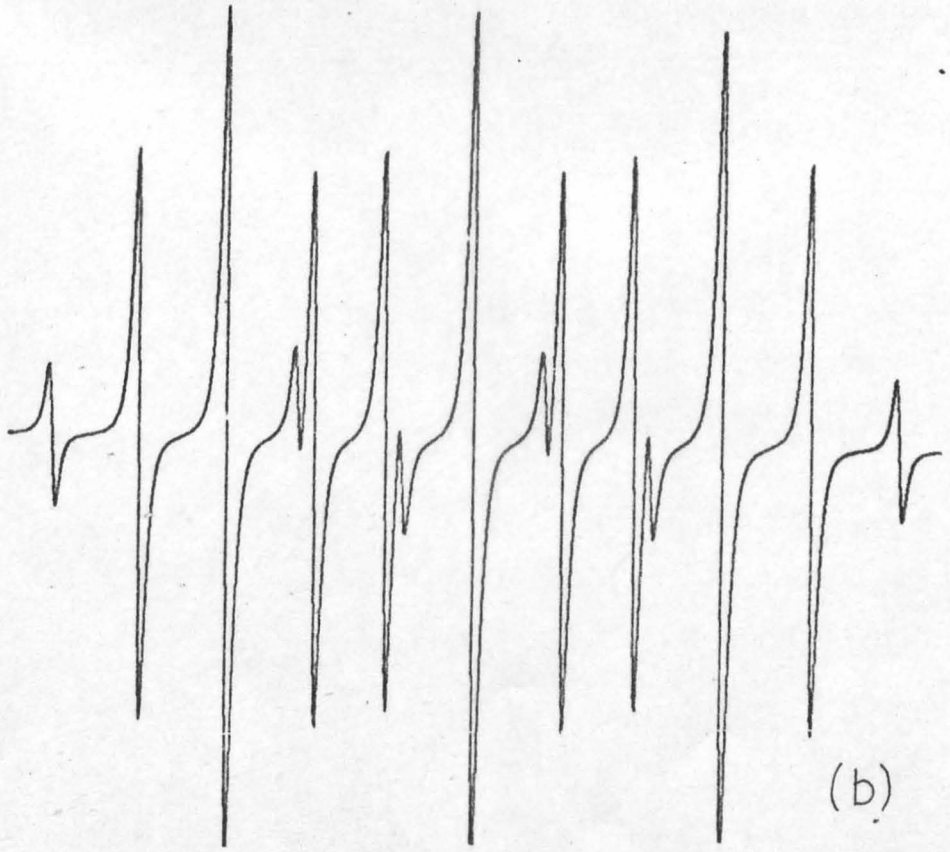
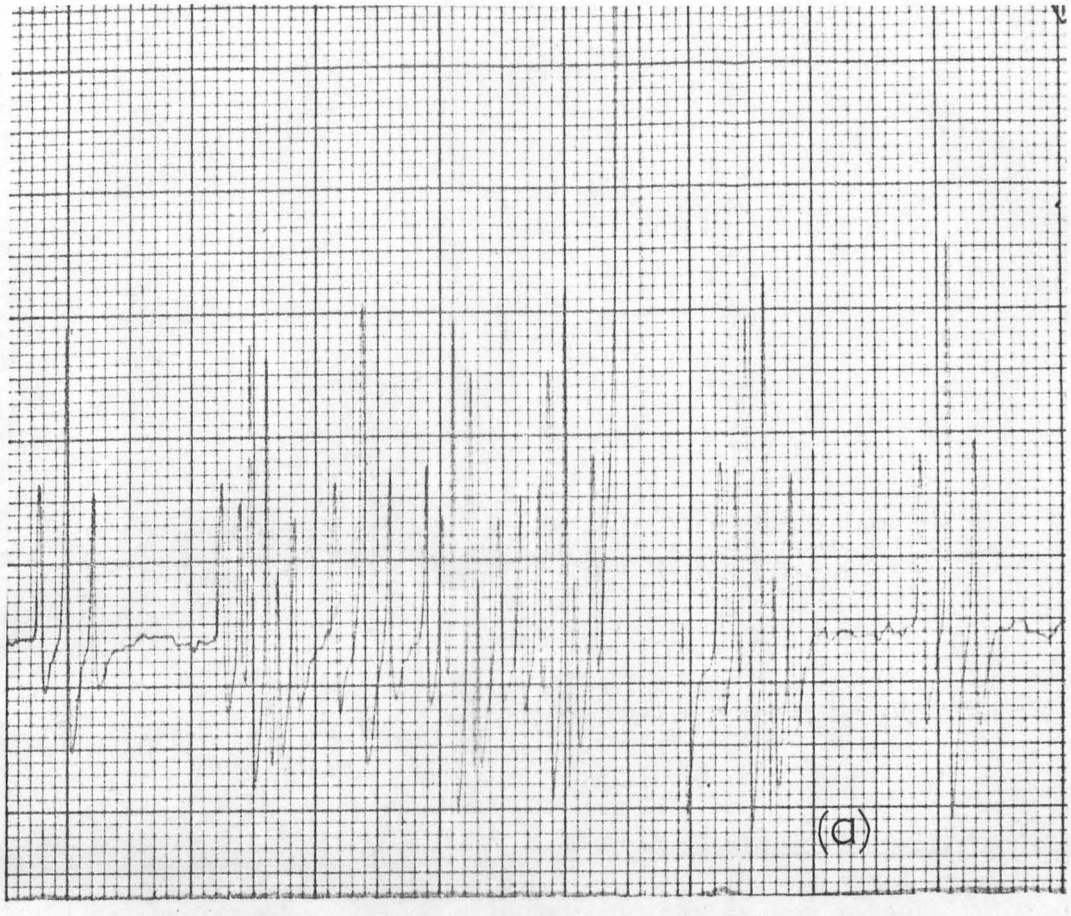

(b)

FIGURE 5.6.

(a) Spectrum from pyridine-2,6-dicarboxylic acid

(b) Computer simulated spectrum


(a)

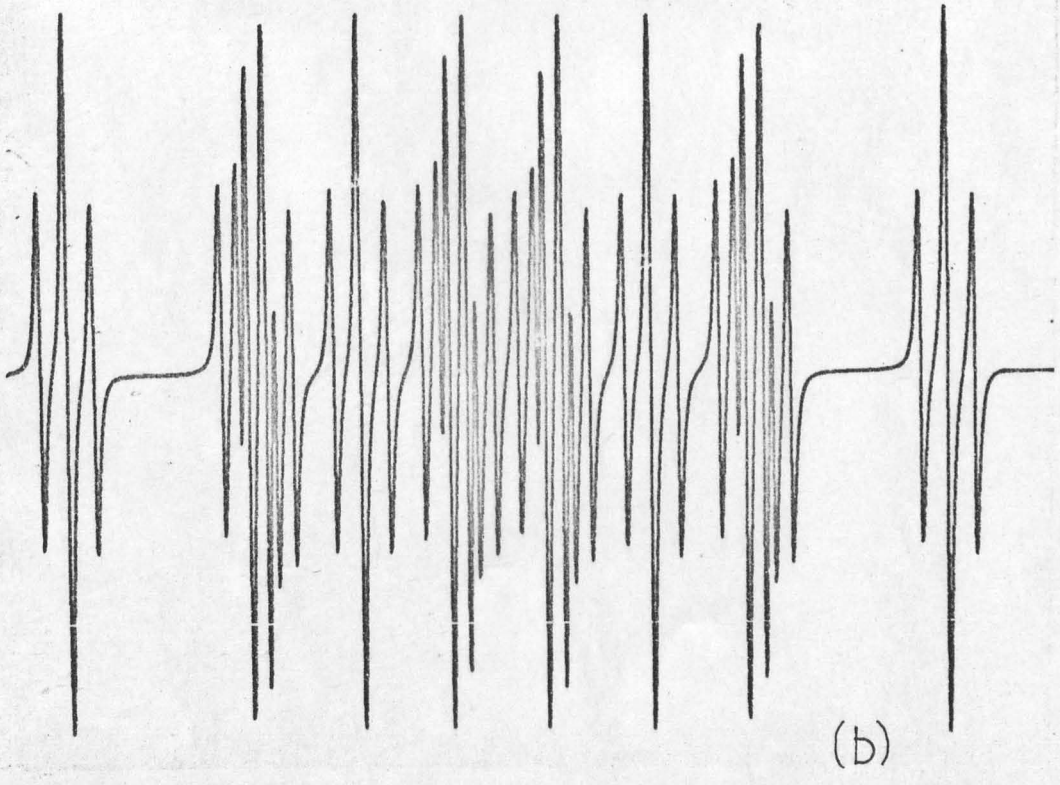
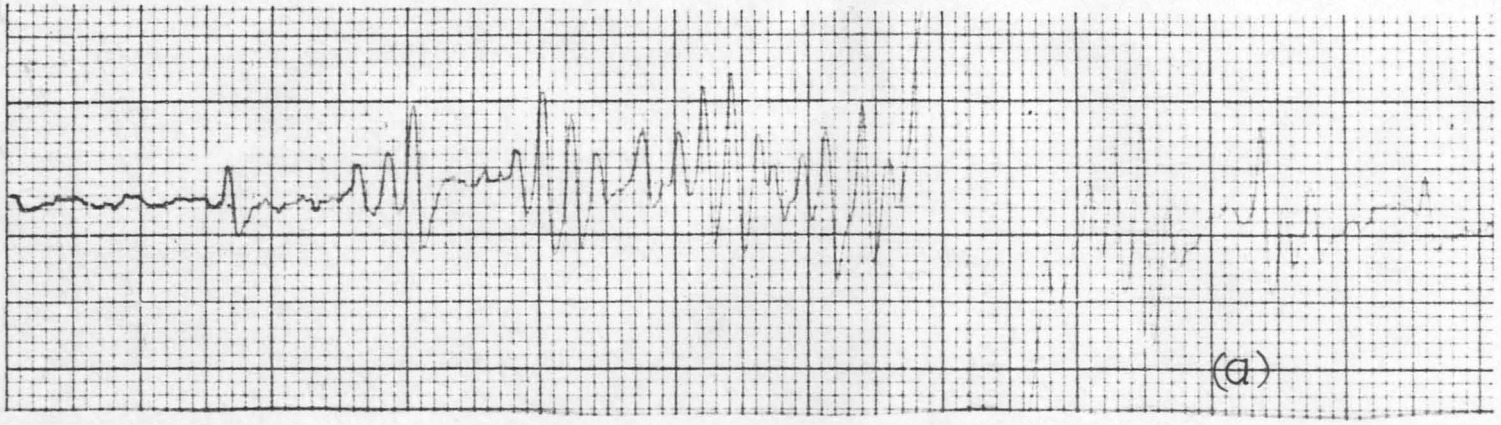

(b)

FIGURE 5.7.

(a) Spectrum from pyridine-3,5-dicarboxylic acid

(b) Computer simulated spectrum



(b)

from the parent acid. The diethyl ester gave a well resolved spectrum showing splittings from four equivalent protons (0.6 oe.), two equivalent protons, a single nitrogen atom and a single proton, but no extra doublet splitting.

Static experiments

None of the mono- or di-acids gave any signal on static reduction. Diethyl dipicolinate gave a multiline spectrum which does not resemble that of the flow reduction, but it has not been interpreted.

5.4. DISCUSSION

5.4.1. Calculation of nitrogen sigma-pi interaction parameters

Once the best value of Q_{CH}^{H} for a series of pyridines and pyrimidines has been determined (see Section 5.4.2. for discussion), the values of the nitrogen sigma-pi interaction parameters Q_{N}^{N} and Q_{CN}^{N} for the series, as defined by the equation

$$a^{N} = Q_{N}^{N} \rho_{N} + Q_{CN}^{N} (\rho_{C} + \rho_{C'})$$

where C and C' are the carbon atoms adjacent to the nitrogen atom, can be determined without direct recourse to MO calculations for estimates of the spin densities ρ_{N}, ρ_{C} and $\rho_{C'}$.[66] Simultaneous solution of the equations defining the nitrogen coupling constants of pyridine and pyrimidine,

$$a_{N} = Q_{N}^{N} [1 - \sum_{i} (a_{CH}^{H_i} / Q_{CH}^{H})] + Q_{CN}^{N} [\sum_{j} (a_{CH}^{H_j} / Q_{CH}^{H})] \quad (1)$$

$$a_{N} = \tfrac{1}{2} Q_{N}^{N} [1 - \sum_{i} (a_{CH}^{H_i} / Q_{CH}^{H})] + Q_{CN}^{N} [\sum_{j} (a_{CH}^{H_j} / Q_{CH}^{H})] \quad (2)$$

(1) and (2) respectively, gives directly the values for Q_{N}^{N} and Q_{CN}^{N}. In

these equations i refers to the carbon atoms of the ring and j to those bonded to the nitrogen atoms. Solution of the equations depends upon the assumption that $\sum \rho = 1$ (ρ summed over all the atoms of the ring) and that coupling constants can be measured for all positions of the ring. The signs, as well as the magnitudes, of the coupling constants are required, but the e.s.r. data give only the magnitudes. Recourse to theory must therefore be made to obtain the signs of the coupling constants in all questionable cases. Simple Hückel and McLachlan treatments show positions 3 and 5 of pyridine, the only doubtful positions, to have positive spin densities. For pyrimidine, the only doubtful positions are 2 and 5; simple Hückel theory places a node at these positions, while McLachlan theory assigns negative spin densities to both positions. Splittings from these two positions are apparent in the e.s.r. spectrum of pyrimidine and evidently the McLachlan treatment represents more accurately the spin distribution in this molecule. Accordingly, positive values for a_{CH}^{H-2} and a_{CH}^{H-5} were taken for equation (2), and negative values for a_{CH}^{H-3} and a_{CH}^{H-5} for equation (1). The Q-values obtained by this treatment are $Q_N^N = 28.5$ oe. and $Q_{CN}^N = -0.5$ oe., in good agreement with data for nitrogen heterocyclics.[19,66,149,159] The experimental spin densities have been determined using these values and are collated in Table 5.3 with the calculated spin densities.

5.4.2. Theoretical calculations

Once experimental coupling constants have been measured, and "experimental" spin densities determined, a comparison can then be made with theoretically calculated spin densities, enabling assignment of coupling constants. For the unsubstituted heterocyclics, pyridine and pyrimidine, the necessary parameters for the MO calculations are the nitrogen Coulomb integral parameter, h_N, and the carbon-nitrogen resonance integral parameter, k_{C-N}, defined as in Chapter 1. In pyridine and pyrimidine each nitrogen atom

TABLE 5.3.

SPIN DENSITIES FOR THE RADICAL-ANIONS OF PYRIDINE AND DERIVATIVES[a]

Substrate	Position	Spin Densities		
		Experimental	Calculated	
			Hückel	McLachlan
Pyridine	N	0.226	0.258	0.273
	2, 6	0.150	0.143	0.148
	3, 5	0.033	0.059	0.011
	4	0.408	0.338	0.408
Pyridine dimer	N	0.143	0.126	0.140
	2, 6	0.023	0.046	0.033
	3, 5	0.114	0.076	0.077
	4		0.130	0.140
Pyridine-N-oxide	N		0.270	0.293
	2, 6	0.128	0.116	0.118
	3, 5	0.018	0.058	0.020
	4	0.361	0.303	0.368
	O		0.080	0.064
Pyrimidine	N[b]	0.122	0.165	0.155
	2	0.032	0.000	-0.028
	4, 6	0.415	0.335	0.398
	5	0.056	0.000	-0.077
4,4'-Bipyrimidine	1	0.112	0.157	0.175
	2	0.067	0.091	0.095
	3		0.004	-0.017
	4		0.106	0.114
	5	0.067	0.089	0.090
	6	0.008	0.054	0.042
2-Methylpyridine	N	0.202	0.239	0.252
	2	0.083[c]	0.089	0.079
	3	0.066	0.106	0.074
	4	0.403	0.333	0.401
	5	<0.004	0.028	-0.029
	6	0.186	0.189	0.212

.....continued

TABLE 5.3. (continued)

Substrate	Position	Spin Densities		
		Experimental	Calculated	
			Hückel	McLachlan
2-Methylpyridine dimer	N	0.097	0.117	0.130
	2	0.021[c]	0.038	0.023
	3	0.116	0.094	0.101
	4		0.131	0.142
	5	0.077	0.064	0.062
	6	0.007	0.050	0.039
3-Methylpyridine	N	0.227	0.259	0.274
	2	0.172	0.185	0.203
	3	0.016[c]	0.039	-0.012
	4	0.407	0.322	0.390
	5	0.057	0.079	0.040
	6	0.113	0.109	0.105
3-Methylpyridine dimer	N	0.129	0.127	0.142
	2	0.088	0.065	0.058
	3	0.068[c]	0.062	0.059
	4		0.120	0.129
	5	0.101	0.083	0.088
	6	0.019	0.034	0.018
4-Methylpyridine	N	0.204	0.246	0.260
	2, 6	0.155	0.144	0.155
	3, 5	0.024	0.044	-0.004
	4	0.403[c]	0.320	0.383
2,3-Dimethylpyridine	N	0.206	0.243	0.258
	2	0.103[c]	0.132	0.132
	3	0.016[c]	0.078	0.039
	4	0.366	0.320	0.388
	5	0.034	0.044	-0.004
	6	0.122	0.147	0.139
2,6-Dimethylpyridine	N	0.174	0.224	0.235
	2, 6	0.112[c]	0.130	0.133
	3, 5	0.030	0.065	0.023
	4	0.393	0.341	0.413

.....continued

TABLE 5.3 (continued)

Substrate	Position	Spin Densities: Experimental	Spin Densities: Calculated Hückel	Spin Densities: Calculated McLachlan
2,6-Dimethylpyridine dimer	N	0.100	0.108	0.120
	2,6	0.010[c]	0.042	0.029
	3,5	0.120	0.082	0.085
	4		0.133	0.144
3,4-Dimethylpyridine	N	0.208	0.247	0.261
	2	0.211	0.189	0.213
	3	<0.007[c]	0.026	-0.027
	4	0.410[c]	0.308	0.369
	5	0.064	0.065	0.025
	6	0.099	0.108	0.107
3,5-Dimethylpyridine	N	0.229	0.264	0.281
	2,6	0.134	0.149	0.158
	3,5	0.037[c]	0.056	0.012
	4	0.375	0.306	0.373
3,5-Dimethylpyridine dimer	N	0.130	0.129	0.145
	2,6	0.024	0.051	0.042
	3,5	0.066[c]	0.069	0.069
	4		0.110	0.118
2-Methoxypyridine	N		0.232	0.243
	2		0.071	0.054
	3	0.046	0.130	0.105
	4	0.302	0.331	0.397
	5	0.019	0.018	-0.043
	6	0.181	0.212	0.241
	O	0.007[d]	0.006	0.001
2,6-Dimethoxypyridine	N		0.217	0.227
	2,6		0.129	0.132
	3,5	0.035	0.073	0.030
	4	0.430	0.361	0.437
	O	0.005[d]	0.010	0.006

.....continued

TABLE 5.3. (continued)

Substrate	Position	Spin Densities		
		Experimental	Calculated	
			Hückel	McLachlan
2,6-Dimethoxypyridine dimer	N		0.105	0.116
	2,6		0.041	0.028
	3,5	9.108	0.084	0.089
	4		0.136	0.148
	O	0.004 [d]	0.004	0.001

[a] "Experimental" spin densities calculated using sigma-pi parameters given in the text;

[b] $a_1 = a_3$;

[c] spin density obtained from methyl proton coupling constant;

[d] spin density obtained from methoxy proton coupling constant.

is assumed to contribute one electron to the pi-system, and parameter values reported in the literature vary as $0.1 \leq h_N \leq 1.0$ and $0.5 \leq k_{C-N} \leq 1.2$.[160] With the McLachlan parameter set at $\lambda = 1.2$, spin densities for pyridine and pyrimidine have been calculated here using the values h_N and k_{C-N} in the ranges quoted above. With all values, the McLachlan treatment produces a large redistribution of spin density, giving rise to large values on the nitrogen atoms with a corresponding increase, compared to simple Hückel spin densities, on the 2- and 4-positions, and a decrease (in sign but not always in magnitude) on the 3-position. For pyridine, with all the values tried, the ortho : para and nitrogen : para ratios of the coupling constants are greater than the corresponding ratios of spin densities. Decrease of the McLachlan parameter λ brings the spin density ratios into better agreement with the coupling constant ratios, and a value of $\lambda = 0.75$ was found to give the best overall agreement with experiment, as suggested by Talcott and Myers.[66] Decrease of the value of λ also improves the agreement between experiment and theory for pyrimidine. For each set of values of h_N and k_{C-N} used, an estimate of Q_{CH}^H was made by comparing coupling constants with the corresponding spin densities, and an estimate of the error in Q_{CH}^H obtained. Parameter values leading to the lowest error in Q_{CH}^H, and also giving good comparison between coupling constant and spin density ratios, suggest the values $h_N = 0.8$ and $k_{C-N} = 1.1$ give the best overall agreement, with $Q_{CH}^H \approx 23$ oe., between theory and experiment.

Once the best nitrogen parameters are known, calculations on the methylpyridines can be made and the best methyl group parameters determined. Two expressions have been obtained theoretically and have been used to relate the methyl group proton coupling constant to the spin density on the contiguous carbon atom, and $Q_{CCH_3}^H$ is the sigma-pi interaction parameter, given the value +28.0 oe. The expression due to Levy,[18] formulated in terms of a hyperconjugation mechanism, is more complex, and leads to no better

agreement with experiment than the simpler equation in the present instance. Throughout this work, therefore, the McLachlan equation has been used to relate methyl proton splitting to spin density. After determination of the best set of methyl group parameters, a plot of $a_{CH}^{H_i}$ vs. ρ_{C_i} was made for pyrimidine and pyridine and its methyl homologues, and the best least-square fit of the equation $a_{CH}^{H} = Q_{CH}^{H} \rho_C$ obtained, giving the best least-squares value of 23.6 ± 0.5 oe. for $\left| Q_{CH}^{H} \right|$.

In determining the methyl proton spin densities the inductive, heteroatom and hyperconjugative models were tried. With the inductive model, conjugation with the ring is neglected, and the inductive effect alone is considered by assigning to the contiguous carbon atom, a small negative h-value, usually in the range -0.3 to -0.5. The heteroatom model assumes the methyl group to behave as a single electron pair on a single atom. Two parameter values are therefore required, a Coulomb integral for the methyl group and a resonance integral for the ring carbon-methyl carbon bond. Parameter values[160] which have been used for h_{CH_3} and k_{C-CH_3} are in the ranges 0.5 to 0.8 and 1.4 to 3.3 respectively, and a number of values within these limits have been tried here. In the hyperconjugative model, the methyl group is assumed to be composed of two parts, the methyl carbon atom and the hydrogen group pseudo-atom, i.e. $\rangle C'-C\equiv H_3$. Several parameters need evaluation here, namely h_C, h_{H_3}, $k_{C'-C}$ and k_{C-H_3}. Values suggested[160] for calculations are

$$h_C = 0 \text{ to } 0.1$$

$$h_{H_3} = 0 \text{ to } -0.5$$

$$k_{C'-C} = 0.7 \text{ to } 1.0 \text{ and}$$

$$k_{C-H_3} = 2.0 \text{ to } 2.5$$

Reasonable agreement between "experimental" and theoretical spin

densities is obtained with the inductive model, the best agreement being with $h = -0.2$. Comparison with experimental values of the spin densities calculated by the heteroatom model, using parameter values in the ranges given above, is poor, with no reasonable agreement using any of the values. The hyperconjugative model gives relatively poor agreement, though better than the heteroatom model, the best set of values being those quoted by Levy,[18] viz. $h_C = -0.1$, $h_{H_3} = -0.5$, $k_{C'-C} = 0.76$ and $k_{C-H_3} = 2.0$.

It has been suggested[161] that to account for the methyl group splitting in the toluene radical-anion, a combination of an inductive and a hyperconjugative effect must be considered. This has been followed here, with the hyperconjugative parameters as given above, and an inductive parameter $h_{Ci} = -0.2$ on the trigonal carbon atom. Better agreement with experiment is found than with either the inductive or hyperconjugative models used alone, and all the methyl coupling constants have been calculated using this combined model with the parameter values given above.

The calculation of spin densities in the pyridine-N-oxide radical-anion involves the evaluation of two extra parameters, the nitrogen-oxygen bond integral parameter, k_{N-O}, and the Coulomb integral parameter for the oxygen atom, h_O. The Coulomb parameter, h_N, for nitrogen will also be different in the N-oxide than in the parent compound due to the different environment of the nitrogen atom. As the nitrogen lone-pair electrons are partially donated to the oxygen atom, leaving a slightly electropositive nitrogen, h_N is expected to be greater than in pyridine itself. Few calculations concerning N-oxides have been reported in the literature, though values used are in the ranges $0.6 \leq h_N \leq 2.0$, $0.7 \leq k_{N-O} \leq 1.0$, $0.6 \leq h_O \leq 1.5$, and an inductive effect of $0.1\, h_N$ on the carbon atoms bonded to the nitrogen has been utilised. Previous e.s.r. studies of aromatic amine N-oxides have suggested the sets of parameter values $h_N = 1.1$, $h_O = 1.5$ or 2.0 and $k_{N-O} = 1.2$,[66] and $h_N = 1.0$, with inductive effect 0.1, $h_O = 0.6$ and $k_{N-O} = 0.8$,[162] and it was

found that the latter set gave the best agreement with experiment for pyridine-N-oxide, with $k_{C-N} = 1.1$ as in the parent pyridine, using $\left| Q_{CH}^{H} \right| = 23.6$ oe.

Correlation of the nitrogen spin density with the corresponding hyperfine coupling constant is made through the equation

$$a_N = Q_N^N \rho_N + Q_{ON}^N \rho_O + Q_{CN}^N (\rho_C + \rho_{C'})$$

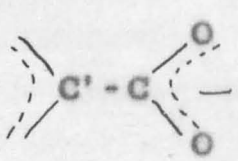
where the terms have their usual significance. Evaluation of the sigma-pi parameters has been attempted in some instances,[66, 162, 163] but little agreement is evident, and little significance could be placed on a calculation based on one species.

Having obtained the nitrogen parameters, methoxy group parameters can be found which give the best fit with experiment. The parameters[160] $h_O = 2.0$ and $k_{C-O} = 0.8$ were chosen and the $-OCH_3$ group was regarded as $-\ddot{O}$, the oxygen atom contributing two electrons to the pi-system. Any inductive effect that the oxygen atom may have on the adjacent ring carbon atom is neglected, and it is assumed that the methoxy-proton coupling constant $a_{OCH_3}^{H}$ is proportional to the spin density ρ_O on the oxygen atom[164]:

$$a_{OCH_3}^{H} = Q_{OCH_3}^{H} \rho_O$$

A value of $Q_{OCH_3}^{H} = 30$ oe.[165] was used to correlate spin densities with coupling constants.

Replacement of hydrogen by a carboxy group effects a considerable change in the spin density distribution. MO calculations were made on the mono- and di-carboxy substituted pyridines using the Coulomb and resonance integral parameters obtained from a study of benzoic acid and its derivatives (see Chapter 6), and are :



$h_O = 2.0$
$k_{C'-C} = 1.2$
$k_{C-O} = 1.6$

Complete ionisation is assumed to occur in both the mono- and di-acids rendering all C-O bonds equivalent. Both Hückel and McLachlan treatments predict that positions para to the carboxy-substituents have large spin densities. Position 6 of pyridine-3-carboxylic acid shows a large coupling constant while that of the nitrogen atom is small, while the nitrogen atom in pyridine-4-carboxylic acid, being para to the substituent, shows a larger splitting. Pyridine-2-carboxylic acid appears to be anomalous, with theoretical spin densities showing little correlation with the coupling constants of the simpler of the two species. It is possible (see below) that the pyridine dicarboxylic acids are N-protonated, and it might be that this is the case with pyridine-2-carboxylic acid also, or that some form of hydrogen bonded species exists. Spin densities have been calculated on this assumption and are given in Table 5.4. In this type of system the nitrogen atom forms a dative bond with a proton, leaving the nitrogen atom partially electropositive, thus requiring a larger value for the Coulomb integral parameter. A value of[160] $h_{NH} = 2.0$ (equivalent to placing a positive charge on the nitrogen atom) was chosen, all other parameters remaining unchanged. Qualitatively, the agreement with experiment seems a little better, though it is far from conclusive that protonation occurs.

The same carboxy group parameters were used in calculating spin densities for the pyridine dicarboxylic acids. Calculations were made on the assumption of N-protonation by setting $h_{NH} = 2.0$, as with pyridine-2-carboxylic acid and C_6H_5NH . For such N-protonated species the expression for the nitrogen coupling constant becomes

$$a^N = (P^{N'} + Q^N_{NH} + 2Q^N_{NC})\rho_N + Q^N_{CN}(\rho_C + \rho_{C'})$$

The term Q^N_{NH} represents all contributions to spin polarisation by the N-H bond, and has the small negative value[19] of -0.4 oe. If $Q^{N'}_N$ is written

TABLE 5.4.

SPIN DENSITIES FOR RADICALS PRODUCED FROM PYRIDINE-ETHANOL AND PYRIDINE CARBOXYLIC ACIDS[a]

Substrate	Position	Spin Densities		
		Experimental	Calculated	
			Hückel	McLachlan
Pyridine-ethanol	N	0.241	0.164	0.150
	2, 6	0.245	0.226	0.266
	3, 5	0.031	0.028	-0.043
	4	0.492	0.328	0.404
Pyridine-2-carboxylic acid	N		0.182 (0.146)[b]	0.206 (0.143)[b]
	2		0.208 (0.240)	0.227 (0.286)
	3		0.062 (0.021)	0.045 (-0.030)
	4	0.230	0.099 (0.192)	0.088 (0.224)
	5		0.183 (0.091)	0.211 (0.067)
	6		0.005 (0.108)	-0.037 (0.105)
Pyridine-3-carboxylic acid	N	0.064	0.050	0.019
	2	0.046	0.055	0.050
	3		0.157	0.152
	4	0.308	0.216	0.259
	5	0.019	0.009	-0.049
	6	0.374	0.278	0.339
Pyridine-4-carboxylic acid	N	0.196	0.192	0.215
	2, 6	0.083	0.071	0.051
	3, 5	0.083	0.115	0.116
	4		0.201	0.218

.....continued

TABLE 5.4. (continued)

Substrate	Position	Spin Densities		
		Experimental	Calculated	
			Hückel	McLachlan
Pyridine-2,3-dicarboxylic acid	N		0.125	0.124
	2		0.304	0.369
	3		0.049	0.013
	4	0.144	0.094	0.099
	5	0.144	0.104	0.098
	6	0.036	0.040	0.019
Pyridine-2,5-dicarboxylic acid	N		0.102	0.097
	2		0.265	0.320
	3	0.067	0.031	-0.019
	4	0.360	0.216	0.256
	5		0.095	0.079
	6	0.038	0.022	0.002
Pyridine-2,6-dicarboxylic acid	N		0.176	0.176
	2, 6		0.183	0.212
	3, 5	0.035	0.003	-0.048
	4	0.384	0.195	0.238
Pyridine-3,5-dicarboxylic acid	N	0.225	0.121	0.106
	2, 6	0.233	0.160	0.187
	3, 5		0.030	-0.029
	4	0.521	0.431	0.543
6-Methylpyridine-2,4-dicarboxylic acid	N		0.131	0.133
	2		0.175	0.202
	3	0.058	0.000	-0.044
	4		0.175	0.193
	5	0.142	0.157	0.163
	6	0.096[c]	0.103	0.101

[a] "Experimental" spin densities calculated using sigma-pi parameters given in the text;

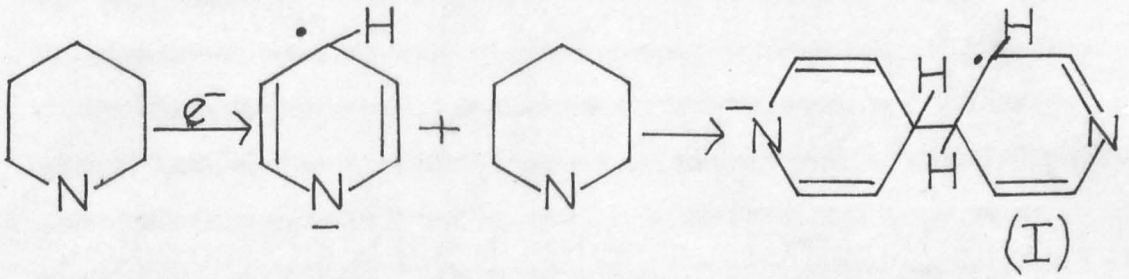
[b] values in parentheses were calculated assuming N-protonation;

[c] spin density obtained from methyl proton coupling constant.

for ($P^{N'} + Q^{N}_{NH} + 2Q^{N}_{NC}$), then a value of 24.6 oe. is obtained using interaction parameters quoted by Stone and Maki,[19] and this value has been used in the present work. Assuming N-protonation to occur, then the coupling constant of the proton bonded to the nitrogen is expected to be proportional to the spin density on the nitrogen atom, and McLachlan[17] has suggested a value of -25 oe. for the sigma-pi parameter relating the nitrogen spin density to the proton coupling constant. Other values have also been used. This enables an independent estimate of the nitrogen spin density to be obtained. The "experimental" nitrogen spin densities for $C_6H_5NH\cdot$ and the pyridine dicarboxylic acids are shown in Table 5.4. It can be seen that calculations based on proton coupling constants give values in better agreement with theory than those obtained using the nitrogen coupling constant, which always produce spin densities much larger than the theoretical predictions. This suggests the interaction parameter $Q^{N'}_{N}$ has too low a value, but in view of the uncertainty in the calculations, alteration would be of questionable value.

5.4.3. Reduction of nitrogen heterocyclics

Flow reductions indicate that generally the reaction between the solvated electron and pyridine, pyrimidine and methyl- and methoxy-substituted pyridines results in the formation of the corresponding monomer radical-anions, which are identified by their characteristic e.s.r. spectra. In the case of pyridine further reaction then occurs to give finally the stable 4,4'-bipyridyl radical-anion, although no further information as to the intermediate steps can be obtained by e.s.r. measurements. In HMPA[144] solution, radical dimerisation is thought to occur to give the dihydrobipyridyl dianion, aromatisation and subsequent one-electron addition giving finally the bipyridyl radical-anion. This is feasible in ammonia, but not necessarily exclusive, as the nucleophilic attack of the pyridine nucleus by the radical-anion may occur,



(I)

4,4'-Coupling appears to be exclusive according to the e.s.r. data. Elimination of H^- from (I) then occurs (possibly through oxidation by trace O_2 impurities) to give bipyridyl.[142a, 144]

Dimerisation is also important in substituted pyridines where the 4-position is not blocked. 2- and 3-Methylpyridines both give dimers but 4-methylpyridine showed no paramagnetic products after decay of the monomer radical-anion. 2,6- and 3,5-Dimethylpyridines both dimerise, as is evident by the spectra obtained a few minutes after the initial mixing. 2,3-Dimethylpyridine gave an uninterpretable spectrum, though it is probably due to the dimer, but 3,4-dimethylpyridine gave no spectrum after the initial reaction, suggesting no dimer formation. It appears that 2-methoxypyridine undergoes dimer formation and 2,6-dimethoxypyridine certainly does, as the e.s.r. spectrum obtained under static conditions unambiguously demonstrates.

Clearly the factors promoting dimerisation are not easy to discern. Dimerisation is most important, if not exclusive, through positions para to the nitrogen atoms. This is evident from the e.s.r. spectra of the symmetrical dimethyl- and dimethoxy-pyridines, as well as pyridine and pentadeuteropyridine, which can only be analysed in terms of highly symmetrical species. Such symmetrical molecules can only be dimers coupled through the 4-positions. If these positions are blocked, dimerisation

is prevented, but a sterically free pyridine such as 2,6-dimethylpyridine can yield monomer radicals stable over a period of minutes. The effects of solvent, temperature, nature of the counter-ion, and ring-substitution all contribute to the several reaction steps between monomer and dimer radical-ions, and more detailed analysis of this problem is required before more definite conclusions can be drawn. Further work is in progress, featuring the imposition of short (100 msec.) delays between mixing and observation, and construction of a double mixing chamber to study the effects of added secondary reactants, and it is hoped that a more detailed understanding of the intermediate steps will be forthcoming.

Some qualitative predictions may be made using some results of the MO calculations, although the results should be treated with some reserve. In pyridine, the spin density is greatest at the 4-position ; hence if radical coupling occurs, greatest overlap of electron density would be achieved at these positions and the activation energy for coupling correspondingly reduced. Again, the calculated bond order for the ring-ring bond in the 4,4'-dimer is greater than in the 2,2'-dimer and thus lends further support to 4,4'-bond formation. Finally, calculations on the free valence indices of the radical-anion also support this conclusion. The 4,4'-dimer permits maximum spatial separation of the electronegative nitrogen atoms, hence electronic repulsion between any negative charge on these atoms will be minimised, giving a system more stable than one in which such spatial separation is not so great.

Analysis of the spectrum obtained on static reduction of pyrimidine suggests dimer formation, but an assignment to a particular dimer from the coupling constants of its radical-anion is difficult, as two different sets of coupling constants produce equally good spectral simulations. The set $a_{4N} = 1.60$, $a_{4H} = 3.17$ and $a_{2H} = 0.20$ oe. indicates a dimer in which all

four nitrogen atoms are equivalent, i.e. 2,2'- or 5,5'-bipyrimidine. Coupling constants for the radical-anion of 2,2'-bipyrimidine are known[159] but are unlike the ones obtained here. Reduction of biphenyl[148] and 4,4'-bipyridyl[142b] indicates that the magnitudes of the coupling constants of the radical-anions are in the order $a_4 > a_2 > a_3$, and the symmetrical bipyrimidine radical-anions might be expected to show a similar trend. This, however, is not the case as the coupling constants indicate a very small triplet splitting due to two equivalent protons, which can only be situated at the 4-positions of a symmetrical dimer. The order of magnitude of the coupling constants, if the 5,5'-dimer is present, is $a_2 > a_3 > a_4$, in contrast to the expected order, and therefore formation of either possible isomeric dimer where the four nitrogen atoms are equivalent is unlikely. Theoretical spin densities for such dimers show no agreement with the coupling constants.

If dimerisation occurs at the position of maximum spin density, then a species such as the 4,4'-dimer is expected. The coupling constants $a_{2H} = 0.20$, $a_{4H} = a_{2N} = 1.57$ and $a_{2N} = 3.14$ oe. are in agreement with this type of dimer, and also reasonable agreement with theoretical spin densities is obtained, as seen in Table 5.3. It is, therefore, suggested that coupling occurs to give 4,4'-bipyrimidine on reduction in ammonia solution.

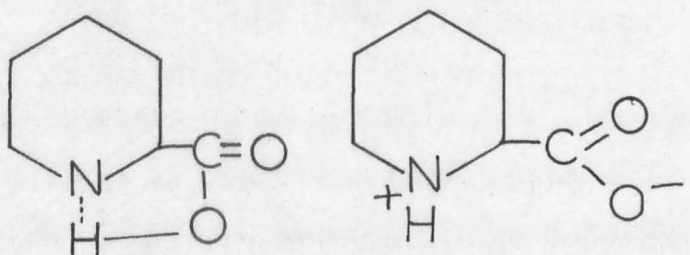
The situation with pyridine-N-oxide is more complex. Reduction first gives the N-oxide radical-anion but this rapidly decays to give a low concentration of the pyridine radical-anion which is present for about 20 minutes. Decay of this species is followed by growth of the 2,2'-bipyridyl radical-anion. It is not clear why the 2,2'-dimer is formed because reduction of pyridine itself gives only the 4,4'-dimer, and the pyridine radical-anion is apparently a precursor of the final product. It has been reported[166] that reduction of pyridine-N-oxide in the presence of ammonium chloride at low temperatures ($< -40^{\circ}C$) gives 44% 2,2'-dimer and very little 4,4'-dimer. Possibly some form of attack by the pyridine radical-anion

on the substrate occurs to give the 2,2'-dimer.

In ammonia, the pyridine-monocarboxylic acids, with the possible exception of the 2-substituted compound, exist in the ionised forms. Reduction of the pyridine-3- and 4-carboxylic acids gives the corresponding radical-dianions, identified by their e.s.r. spectra. The situation with pyridine-2-carboxylic acid is more complex, and it is possible that the nitrogen atom may be bonded to some extent to the carboxy proton. This is suggested by pK_a measurements, the values for the three monocarboxylic acids being[167]

pyridine-2-carboxylic acid	pK_a 4.12
pyridine-3-carboxylic acid	pK_a 3.75
pyridine-4-carboxylic acid	pK_a 3.44

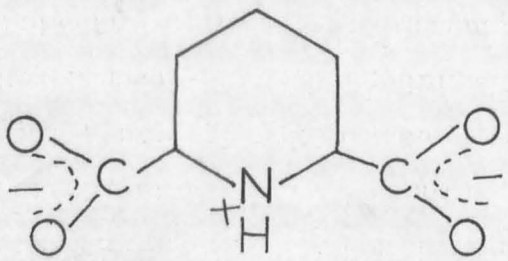
Calculations show that positive charge is greatest at the 2-position of pyridine, and so the 2-substituted acid would be expected to be the strongest. The higher pK_a for this acid may possibly be due to the proximity of the nitrogen to the carboxyl proton, as it is possible that the carboxyl group could be orientated so the proton is near the electronegative nitrogen atom. Observations on the rate of decarboxylation of the 2-carboxypyridine suggest that the reactive form is a hydrogen bonded species, or more likely a zwitterion,[168] i.e. (II) rather than (I) :



(I) (II)

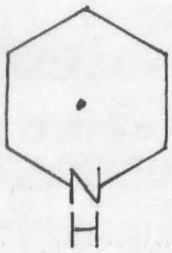
The one noticeable feature of the e.s.r. spectra of the pyridine-dicarboxylic acid reduction products is a doublet splitting extra to the expected number. Analysis of the spectra from the symmetrical pyridine-2,6-

and 3,5-dicarboxylic acids shows that the doublet cannot arise from a proton attached to a carboxyl group, as this would cause a perturbation of the symmetry of the molecule. This is not the case as splittings from two equivalent ring protons are observed in both instances. Proton splittings on a carboxyl group are generally too small to be observed,[62,169] and exchange mechanisms are unlikely to give the observed spectra, where the doublet splittings are 5.63 and 9.07 oe. for the 2,6- and 3.86 and 12.31 oe. for the 3,5-dicarboxypyridines. If the origin of the extra doublet splitting is the carboxyl groups, then substitution of the carboxyl protons should remove this splitting. Accordingly, the diethyl ester of 2,6-dicarboxypyridine was prepared, and reduction gave a spectrum showing no extra doublet splitting, but in addition, a splitting due to four equivalent protons, arising from the α-protons of the ethyl group. These observations suggest the extra doublet splitting in the acid is caused by the acidic protons which are ionised from the carboxy groups. A proton is then attached to the heterocyclic nitrogen to give a zwitterion type structure



the paramagnetic species being due to the one-electron reduction product. The phthalic acids show no extra doublet splitting (Chapter 6), pointing to the necessity of an electronegative atom in the ring to stabilise the proton.

N-protonation is also believed to be responsible for the change of spectrum which occurs when ethanol is introduced into the reacting system with pyridine as substrate yielding the radical



This neutral species shows coupling constants in reasonable agreement with those recorded by Chacaty[170] who obtained a much less well-resolved spectrum by γ-radiolysis of frozen solutions of pyridine in ethanol, but contrasts with the interpretation of an identical spectrum obtained by David et al.,[171] obtained by γ-irradiation of pyridine in methanol at 77°K, who suggest the formation of the 2-pyridyl radical. An alternative structure is a cyclohexadienyl type sigma-radical which has been postulated as arising from addition of a hydrogen atom to pyridine,[172,173] but this is unlikely because of the similarity of the coupling constants to pi-type radicals and to the pyridine radical-anion.

It has been shown[174] for the p-phenylene-diamine cation that $a^N/a^H_{NH} = -1.12$; for the protonated species reported here, i.e. $C_5H_5NH^{\bullet}$ and the dicarboxylic acids, this relationship is fairly closely followed, as is apparent from Table 5.5. This behaviour is expected if the proton coupling constant is proportional to the pi-electron spin density on the nitrogen atom, although the deviations suggest some other contributions affecting the proton couplings.

The coupling constants of the deuterium substituted pyridine and 4,4'-dimer are entirely consistent with theory. The isotropic coupling constant of an atom is proportional to its magnetic moment, and the ratio of the deuteron : proton moments is $g_D/g_H = 0.1513$.[175] The deuterium coupling constants should be correspondingly reduced from the respective proton values, all other coupling constants being unchanged, and this is indeed the case, the deuterium coupling constants being reduced while the nitrogen splittings are little changed.

TABLE 5.5.

RATIO OF THE NITROGEN : PROTON COUPLING CONSTANTS IN THE N-PROTONATED SPECIES

Substrate	Coupling Constants (oersted) a^N	a^H_{NH}	a^N / a^H_{NH}
Pyridine-ethanol	5.79	4.21	1.37
Pyridine-2-carboxylic acid	4.1	4.1	1.0
Pyridine-2,3-dicarboxylic acid	0.85	0.85	1.0
Pyridine-2,5-dicarboxylic acid	4.22	4.68	0.90
Pyridine-2,6-dicarboxylic acid	6.16	5.63	1.09
Pyridine-3,5-dicarboxylic acid	4.78	3.86	1.24
6-Methylpyridine-2,4-dicarboxylic acid	5.05	4.03	1.25

CHAPTER 6

REDUCTION OF AROMATIC CARBOXYLIC ACIDS

6.1. INTRODUCTION

The reduction of substituted benzoate ions

$$X - C_6H_4 - CO_2^- + e^-_{solv} \rightarrow X - C_6H_4 - CO_2^{2-} \quad (1)$$

(X ≡ H, CH_3, CH_3O, CO_2^-, CN, NO_2) has been examined and the second-order rate constant for the reaction (X ≡ H) has been shown by pulse radiolysis to be 3.1×10^9 l.mole.$^{-1}$ sec.$^{-1}$ and comparable rates are found[176,177] for X ≡ NH_2, CH_3, F, Cl, Br, I, CN, CO_2^-. The characteristic optical spectrum obtained from pulse radiolysis of isophthalate ion was reduced by the addition of nitrous oxide, an electron scavenger, which suggests the phthalate ion transient is a species formed by capture of the hydrated electron, such as radical-anions or protonated forms of these.

Preparation of radical-anions of carboxylic acids by electrolytic reduction is successful only when X is electronegative, for example, CN,[126] NO_2,[113,178] or CO_2R[179]; however, simple esters,[154,179-182] for example methyl benzoate, can be reduced by this means to give well-resolved e.s.r. spectra. Electron attachment to benzoic acid has been accomplished by means of the rotating cryostat technique[183] but the resulting e.s.r. spectra show extensive line-broadening due to the use of solid matrices.

The products of reduction of sodium benzoate by a solution of sodium in liquid ammonia, in the absence of a proton donor, is a dihydro derivative.[101,184] A similar reduction of benzoic acid in the presence of methanol[185] or ethanol[186] gives 1,4-dihydrobenzoic acid. This isomer is identified by the lack of ultra-violet absorption which would be expected for structures in which the double bonds are conjugated either with each other or with the carboxyl group. Reduction of o-toluic[187] and o-anisic[188] acids with sodium in ammonia, in the presence of a proton source, gives the corresponding

1,4-dihydroacids. Tetrahydroacids are obtained from p-toluic and m-anisic acids.[186]

6.2. EXPERIMENTAL

When the acids were sufficiently soluble, substrate concentrations were made up to 10^{-2} M in each case. 5-Nitrophthalic acid and benzene-1,3,5-tricarboxylic acid were only sparingly soluble in ammonia and ammonia with 10% v/v of tetrahydrofuran. Phthalic acid remained insoluble on adding tetrahydrofuran to ammonia.

Maximum flow rates were employed in all cases. A delay of 1.0 sec. between mixing and observation was employed in some cases to enable detection of any secondary species. Static experiments were performed in the usual manner (Chapter 3).

Materials

All the materials were commercial products and were purified before use by distillation or recrystallisation, where necessary. The spectrum obtained on the reduction of p-chlorobenzoic acid was identical to that of the p-nitrobenzoic acid radical-anion. The purity, quoted as 99%, was checked by G.L.C. and proton n.m.r. but p-nitrobenzoic acid was not detected.

6.3. RESULTS AND ANALYSIS OF SPECTRA

With the exception of the nitro-substituted acids, the coupling constants for all the radicals are given in Table 6.1.

Flow experiments

Reduction of benzoic acid at 10^{-2} M gave a well-resolved spectrum showing splitting from two groups of two equivalent protons, and a single proton. The experimental and simulated spectra are shown in Figure 6.1. This suggests a radical of the type $C_6H_5CO_2^{2-}$, the simple one-electron reduction product of the benzoate ion. The species is not observed 1.0 sec.

TABLE 6.1.

COUPLING CONSTANTS FOR RADICAL-ANIONS PRODUCED FROM BENZOIC ACID AND DERIVATIVES[a]

Substrate	Coupling Constants (oersted) a_2	a_3	a_4	a_5	a_6	g-value
Benzoic acid	4.24[b]	0.81[c]	7.78			2.0034
Isophthalic acid	1.21		6.87[d]	3.03		2.0034
Terephthalic acid	1.69[e]					2.0039
2-Methylbenzoic acid	4.32[f]	0.73	8.90	1.02	4.65	2.0031
3-Methylbenzoic acid	4.42	0.93[f]	7.47	0.72	4.02	2.0034
4-Methylbenzoic acid	4.96[b]	1.16[c]	9.18[f]			2.0037
3,4-Dimethylbenzoic acid	5.18	0.97[f]	9.07[f]	0.89	4.86	2.0022
3,5-Dimethylbenzoic acid	4.13[b]	0.80[c,f]	7.12			2.0034
4-Methoxybenzoic acid	4.84[b]	1.29[c]	0.32[g]			2.0029
3-Fluorobenzoic acid	4.63	3.22[h]	7.26	0.27	3.22	2.0032
4-Fluorobenzoic acid	4.68[b]	1.19[c]	17.45[h]			2.0037
Thiobenzoic acid	4.02[b]	1.14[c]	5.53			2.0046

[a] Assignments indicated based on MO calculations ;

[b] $a_2 = a_6$;

[c] $a_3 = a_5$;

[d] $a_4 = a_6$;

[e] $a_2 = a_3 = a_5 = a_6$;

[f] methyl proton splitting ;

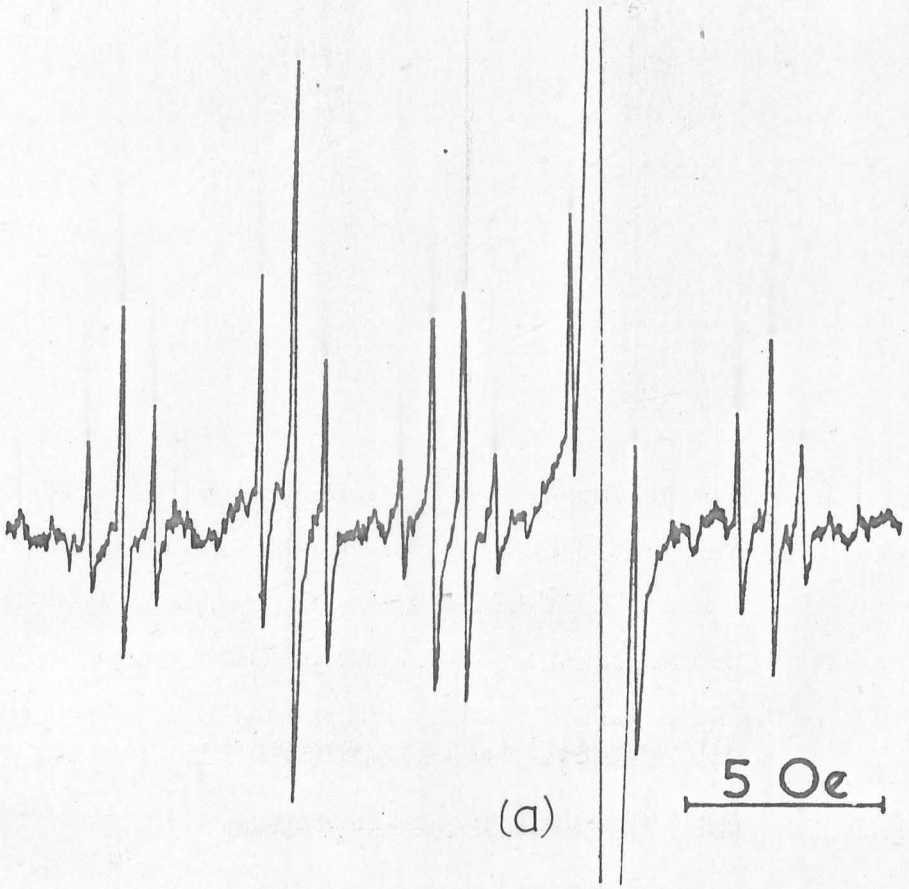
[g] methoxy proton splitting ;

[h] fluorine splitting.

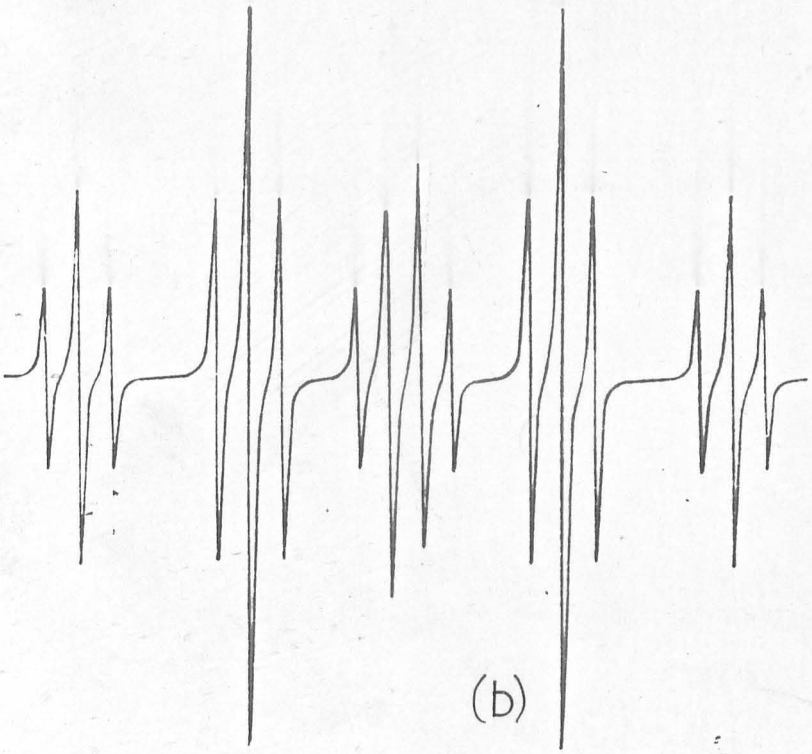
FIGURE 6.1.

(a) Spectrum from benzoic acid

(b) Computer simulated spectrum



(a)



(b)

after mixing. Isophthalic acid gave a 12-line spectrum, the number expected from the one-electron reduction product. These are grouped in three sets of four lines, the two outer sets being of the same height and width, but the inner set of four lines are of greater width and lower amplitude. Terephthalic acid gave a spectrum of 5 lines with intensities in the approximate ratio 1 :4 :6 :4 :1, expected if the 4 ring protons are equivalent. An insoluble product is formed in this reaction which tended to restrict the mixer unless very high flow rates were used. Saturated solutions of phthalic acid and benzene-1,3,5-tricarboxylic acid were run, but no spectra were obtained.

The three methyl benzoic acids all gave spectra in accord with expectation, splittings from each ring proton and the three methyl protons being evident in each case. The coupling constants are in good agreement with those of benzoic acid itself, and serve to confirm the assignments based on MO calculations. The spectra of the m- and p-toluic acids are shown in Figures 6.2 and 6.3. respectively.

Anisic acid (p-methoxybenzoic acid) gave a well-resolved spectrum showing methoxy proton splittings, analysis being straightforward in terms of two non-equivalent groups of two protons, and four equivalent protons.

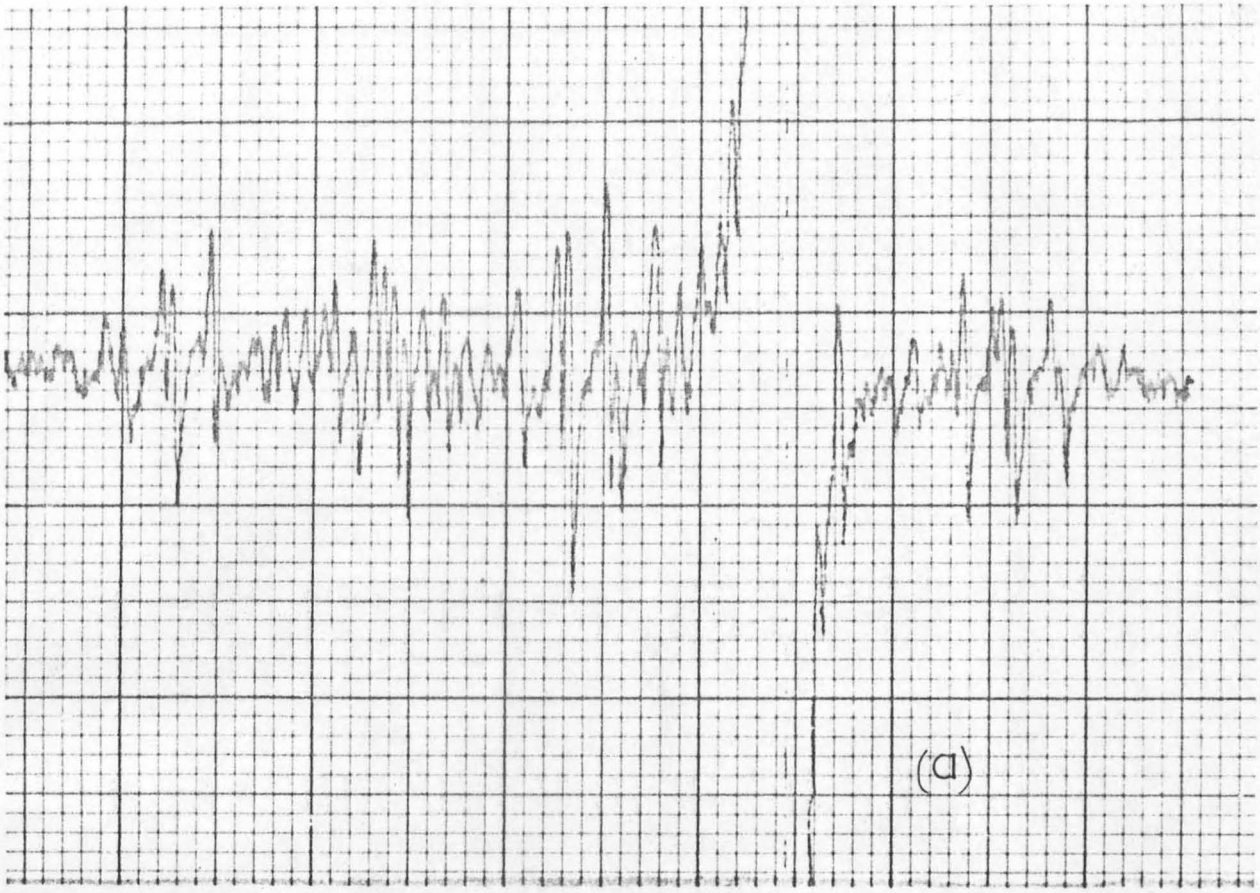
Two dimethyl substituted acids, 3,4- and 3,5-dimethylbenzoic acids gave good spectra on reduction, the coupling constants being in good agreement with those of the parent acid. The small methyl proton coupling constants evident in the 3,5-dimethylbenzoic acid spectrum show the 3-position to have the smaller of the splittings from the 2- and 3-positions. The spectrum obtained from 3,5-dimethylbenzoic acid is shown in Figure 6.4.

Reduction of o-chlorobenzoic acid gave 5 broad lines which occur at the same field values as the groups in the benzoic acid spectrum. The quality of the spectrum could not be improved, and it is impossible to decide if the spectrum is due to benzoic acid itself. No signal was obtained from m-chlorobenzoic acid, although the blue colour due to e^-_{amm} was absent on exit of the

FIGURE 6.2.

(a) Spectrum from 3-methylbenzoic acid

(b) Computer simulated spectrum



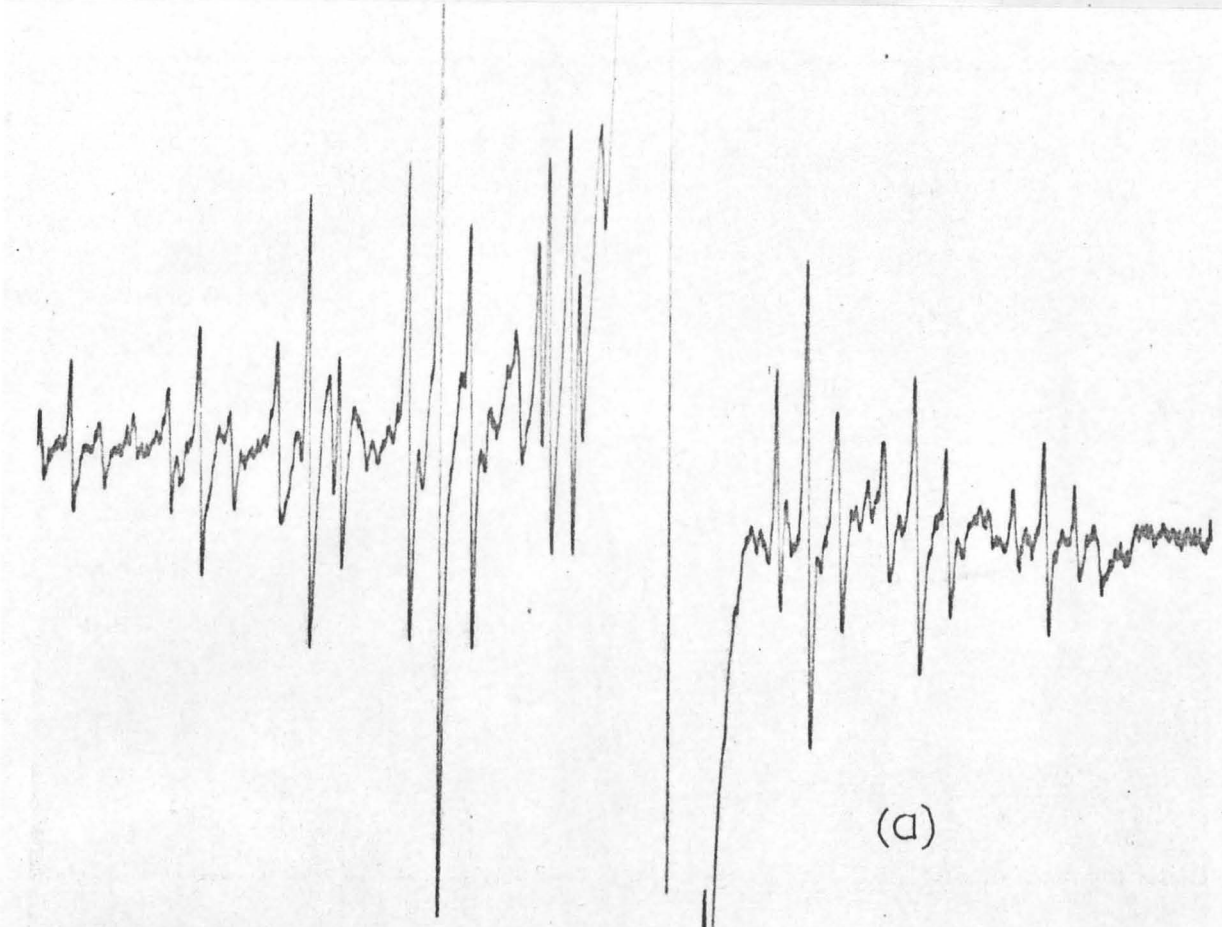
(a)

(b)

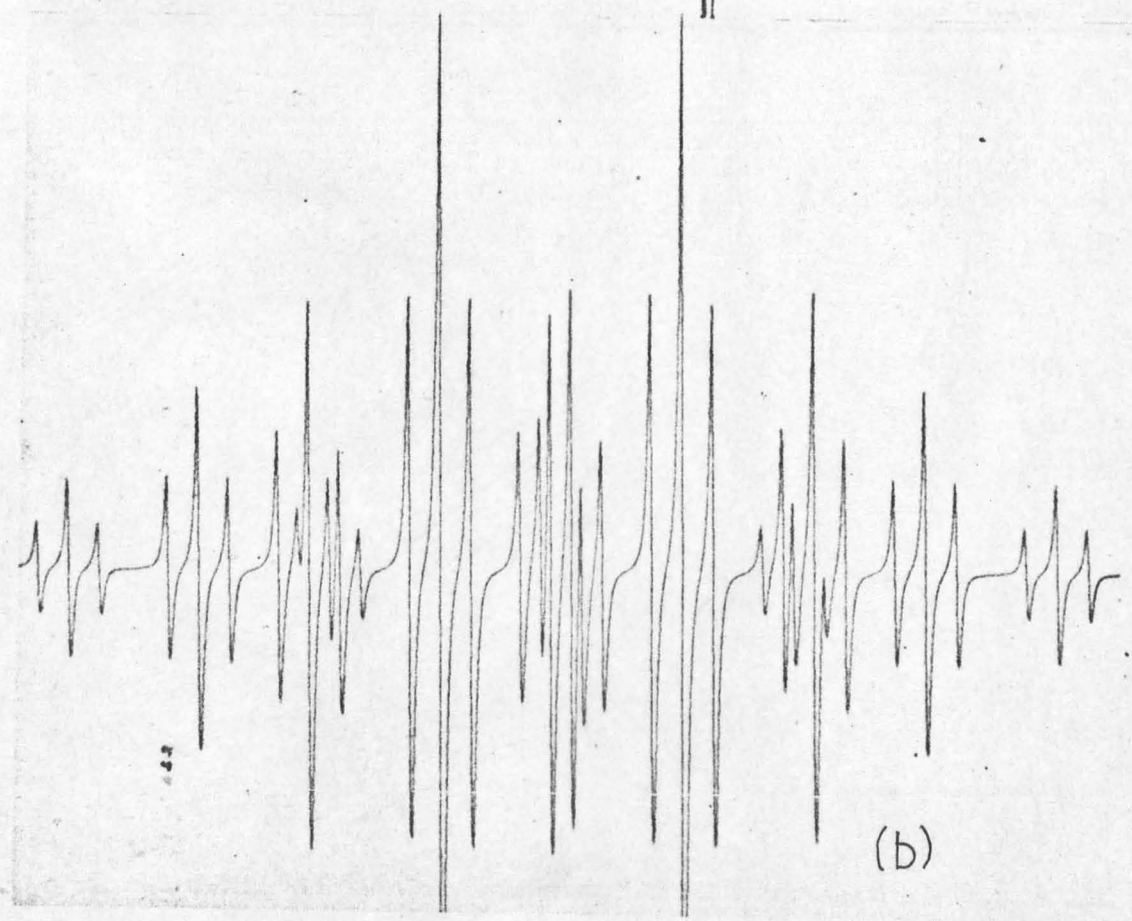
FIGURE 6.3.

(a) Spectrum from 4-methylbenzoic acid

(b) Computer simulated spectrum



(a)

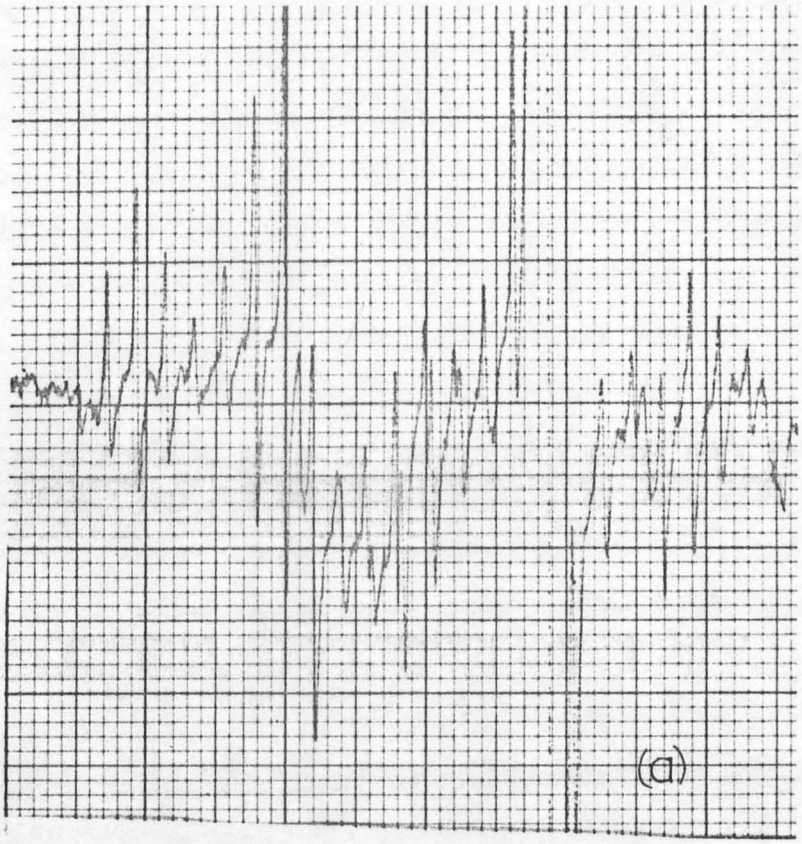


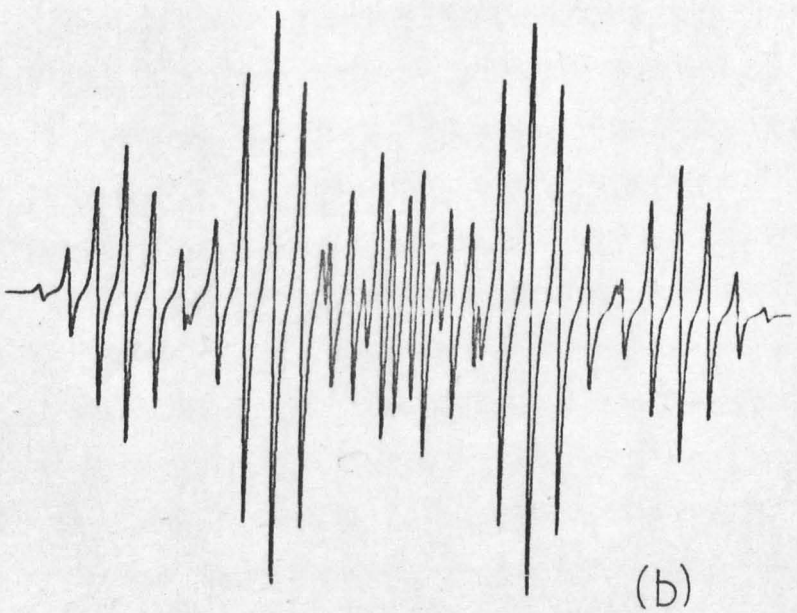
(b)

FIGURE 6.4.

(a) Spectrum from 3,5-dimethylbenzoic acid

(b) Computer simulated spectrum


(a)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solution from the cavity. p-Chlorobenzoic acid gave a single spectrum identical to that obtained from p-nitrobenzoic acid, and it is possible that electron-transfer from the chloro acid to a trace nitro impurity is occurring (cf. Chapter 4). The signal intensity was low, indicating a low concentration of the radical responsible for the signal. 2-Chloro-4-toluic acid gave no signal. p-Bromobenzoic acid gave a low intensity signal composed of 4 broad peaks and a broad e^-_{amm} line. Superposition of this spectrum on that of benzoic acid showed the coincidence of the broad lines with the benzoic acid groups. m-Iodobenzoic acid gave a 5-line spectrum similar to that from o-chlorobenzoic acid and it is possible that it is due to benzoic acid itself, although correct analysis is impossible. Computer simulations using a line width of 0.7 oe. gave comparable, though not identical, spectra. p-Iodobenzoic acid gave no detectable e.s.r. signal.

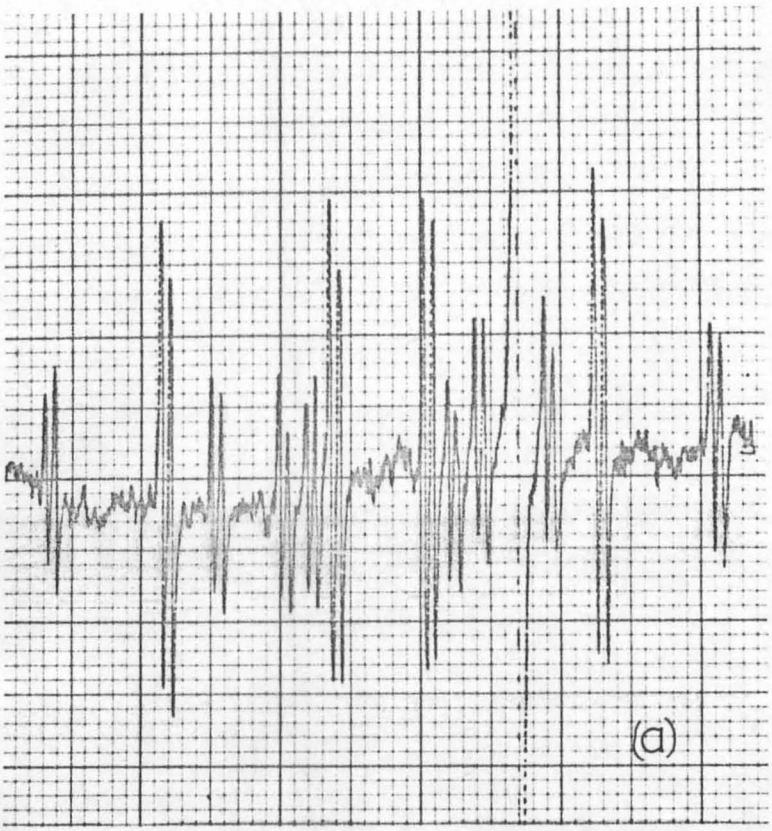
o-Fluorobenzoic acid gave a small spectrum with relatively broad lines (line width 0.5 oe.), showing a doublet of triplets, the two innermost lines being almost superimposed. The coupling constants are 11.0 and 4.4 oe. for the doublet and triplet respectively.

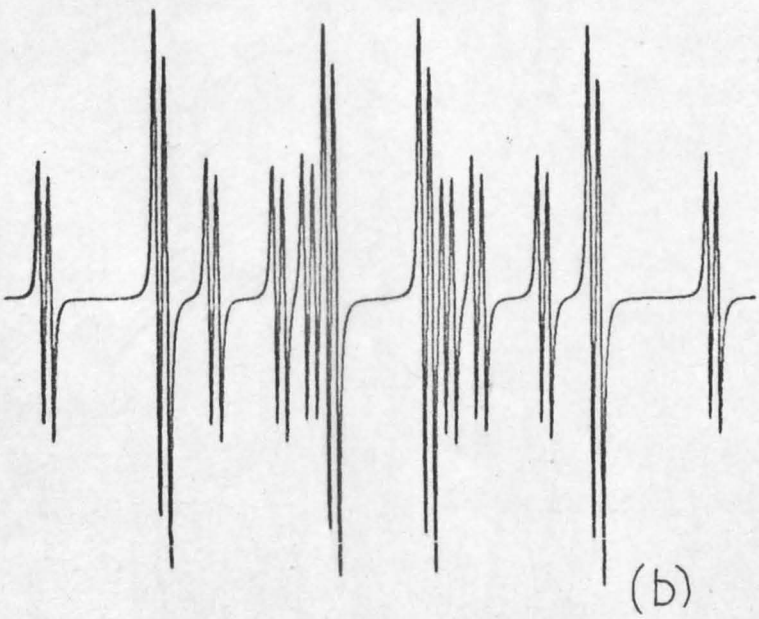
A well-resolved spectrum was obtained from m-fluorobenzoic acid, which is analysed in terms of doublet splittings from three non-equivalent positions and a 1 :2 :1 triplet from two equivalent positions. The coupling constants are presented in Table 6.1 and the spectrum illustrated in Figure 6.5. The spectrum obtained on reduction of p-fluorobenzoic acid is clearly due to two different species, one being in excess of the other. The two spectra show different g-values, the separation between the centres of the spectra being 0.41 oe. Comparison with the spectrum of the benzoate radical demonstrates the most intense signal is due to this species, it possessing the lower g-value. The lower-intensity spectrum is analysed in terms of two 1 :2 :1 triplets with splittings of 4.68 and 1.19 oe., and a doublet splitting of 17.45 oe. Maximum flow rates were employed, but failed to enhance the intensity of

FIGURE 6.5.

(a) Spectrum from 3-fluorobenzoic acid

(b) Computer simulated spectrum


(a)


(b)

the latter species. Observations performed 1.0 sec. after mixing gave no signal. The experimental and simulated spectra, using the coupling constants of Table 6.1, are shown in Figures 6.6 and 6.7.

Reduction of p-nitrobenzoic acid was performed in the flow system, although the stability of the reduced product permits its observation by static methods, in order to check the coupling constants with those obtained previously. Good agreement is found, as can be seen from Table 6.2., although the nitrogen coupling constant is different, presumably due to solvent effects. Nitroterephthalic acid gave a well-resolved spectrum which is analysed in terms of splittings from a single nitrogen atom, non-equivalent doublets from two protons and a 1 :2 :1 triplet from two equivalent protons. The spectrum is shown in Figure 6.8. Reduction of 5-nitroisophthalic acid gave a spectrum composed of two species of identical g-values, one species more intense than the other. The less intense species is analysed in terms of splittings from a single nitrogen nucleus, two equivalent protons, and two non-equivalent protons, while the more stable species is due to a compound with a single nitrogen nucleus, two equivalent protons and a single proton. The spectra are shown in Figure 6.9.

Thiobenzoic acid gave a well-resolved spectrum interpreted in terms of splittings from two non-equivalent groups of two protons, and a single proton. The spectrum is shown in Figure 6.10., and the coupling constants are given in Table 6.1. Dithioterephthalic acid gave a spectrum showing 5 main broad lines separated by ca. 3 oe., with some hyperfine structure superimposed upon each line. The reason for this additional splitting is not clear.

Static experiments

With the exception of the compounds mentioned below, the acids gave no detectable e.s.r. signals on observation about a minute after mixing. Nitroterephthalic acid gave a spectrum which is interpreted as arising from

TABLE 6.2.

COUPLING CONSTANTS FOR RADICALS PRODUCED FROM NITRO-SUBSTITUTED ACIDS[a]

Substrate	Position	Coupling Constants (oersted) Flow	Static
4-Nitrobenzoic acid	N	10.78	
	2, 6	1.11	
	3, 5	3.33	
4-Nitrobenzoic acid[a]	N	12.3	
	2, 6	1.1	
	3, 5	3.4	
Nitroterephthalic acid[c]	N	9.21	8.12
	3	3.26	3.77[d]
	5	3.26	3.92[d]
	6	0.98	1.01
	H[e]	12.19	
5-Nitroisophthalic acid	N	9.23	12.05
	2	2.90	3.75
	4, 6	3.34	3.41
	H[e]	12.05	

[a] Assignments indicated based on MO calculations;

[b] values from ref. 5;

[c] flow reduction assignments uncertain for nitroterephthalic acid;

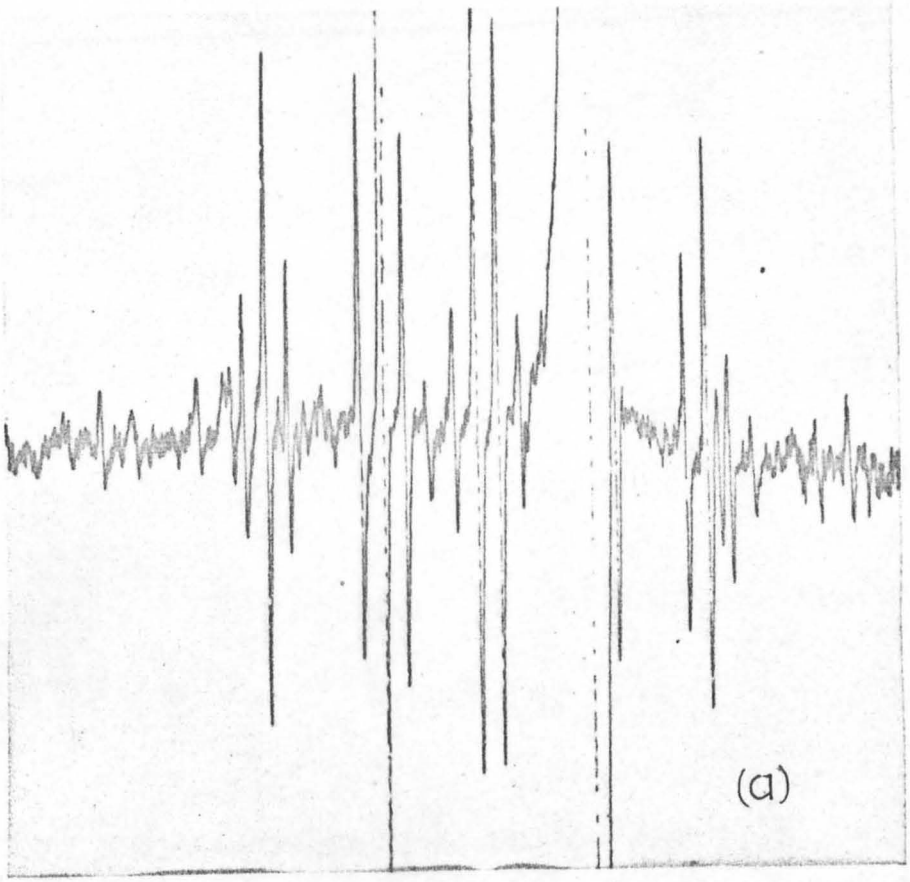
[d] assignment of these two coupling constants is uncertain;

[e] extra doublet splitting observed on flow reduction.

FIGURE 6.6.

(a) Mixed spectrum from 4-fluorobenzoic acid

(b) Computer mixed spectrum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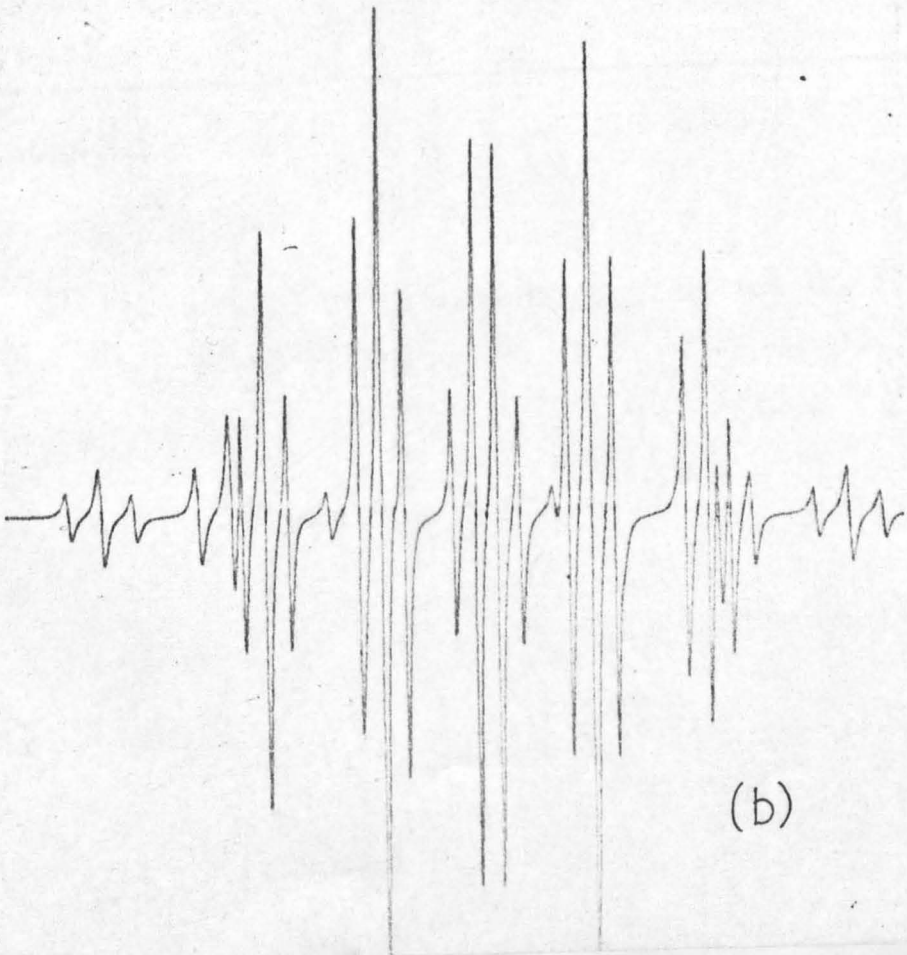
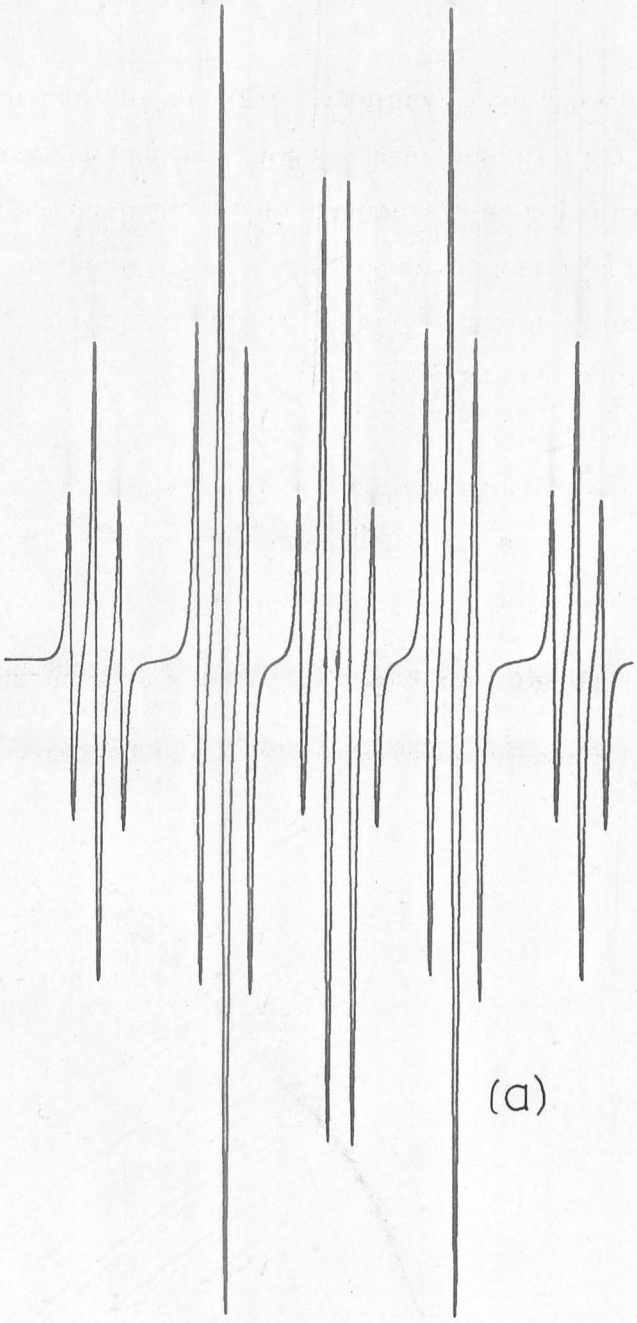

(b)

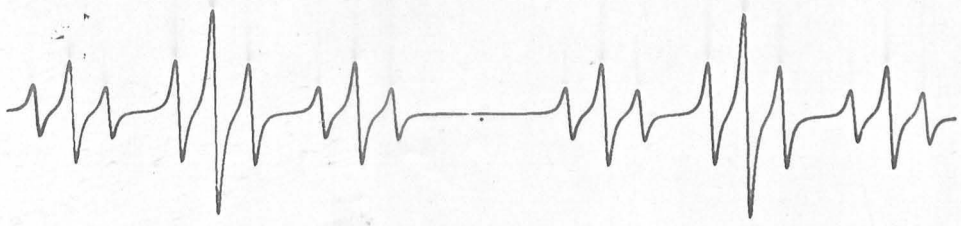
FIGURE 6.7.

(a) Computer simulated spectrum of benzoic acid

(b) Computer simulated spectrum of 4-fluorobenzoic acid



(a)

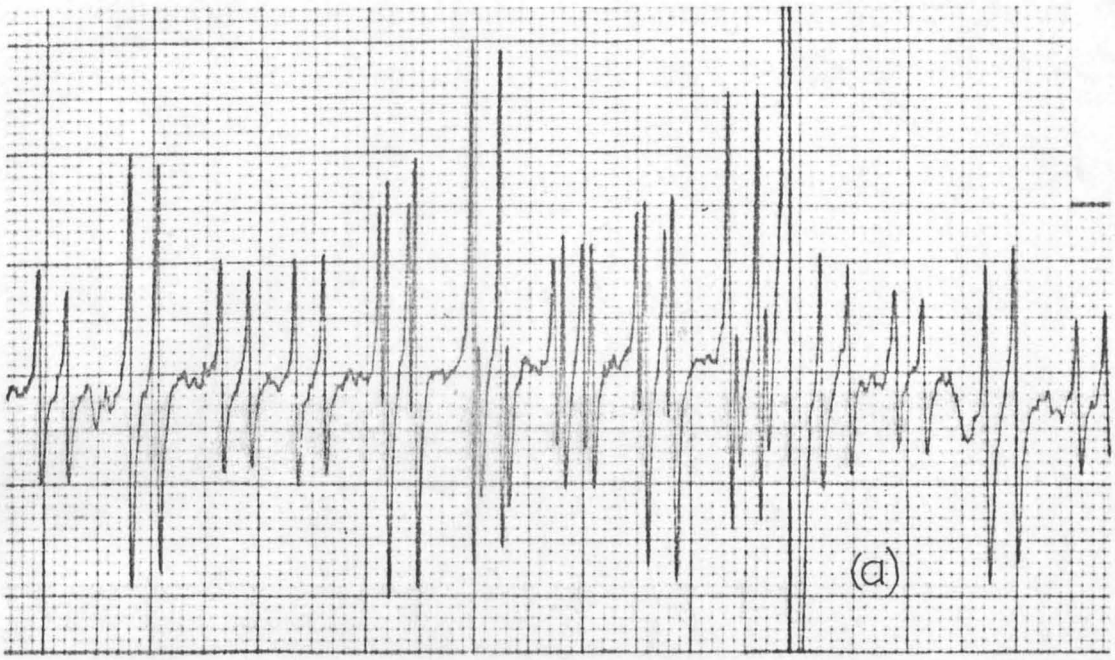


(b)

FIGURE 6.8.

(a) Spectrum from nitroterephthalic acid

(b) Computer simulated spectrum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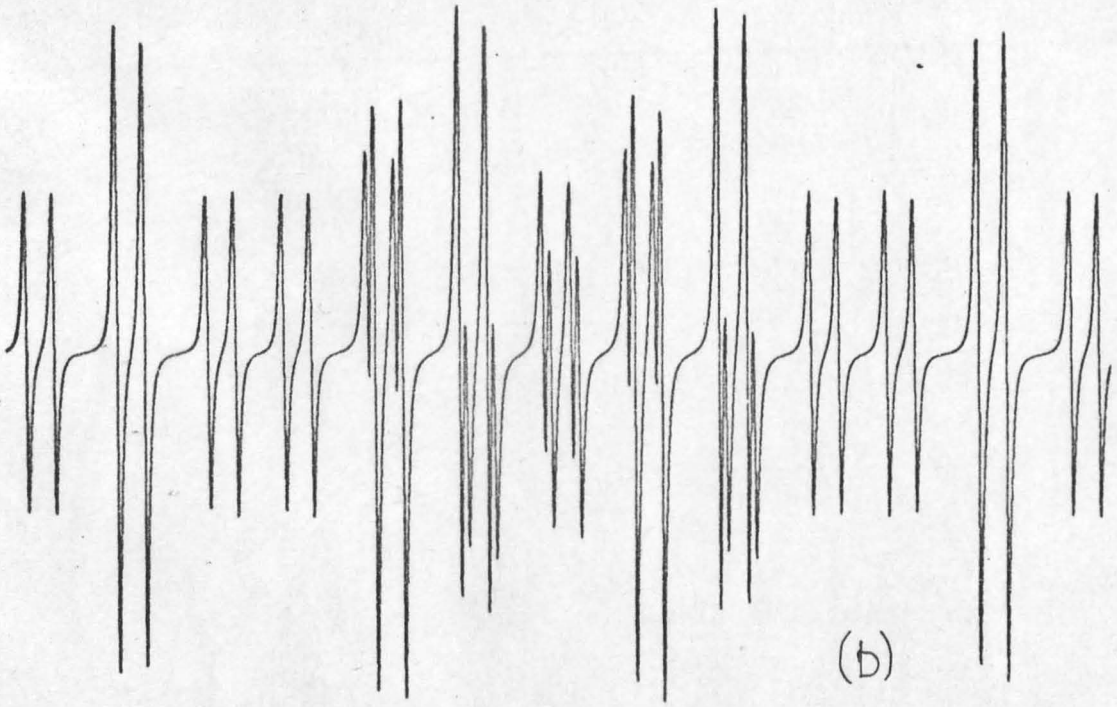
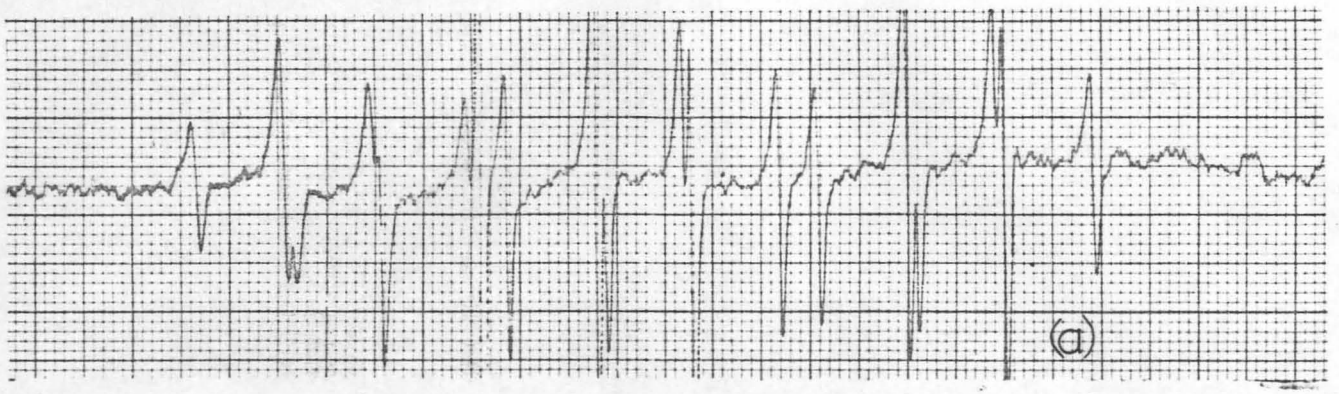

(b)

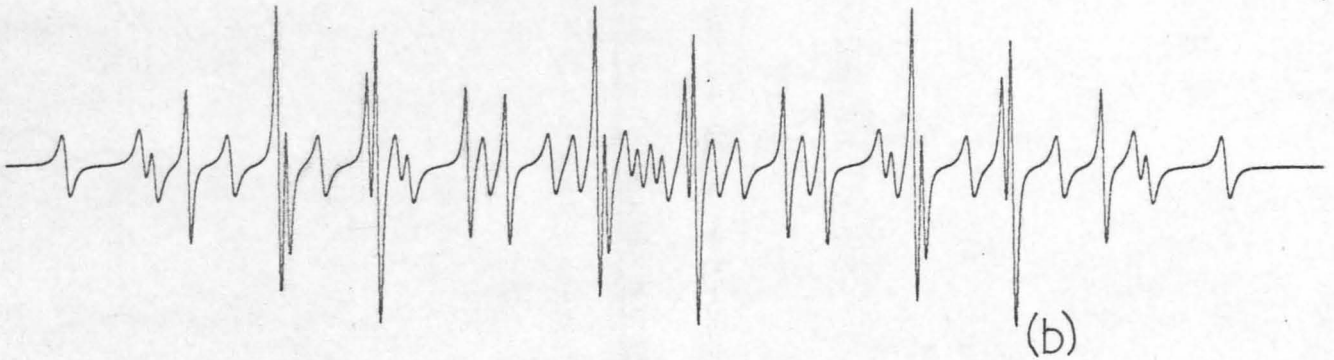
FIGURE 6.9.

(a) Spectrum from static reduction of 5-nitroisophthalic acid

(b) Computer simulated mixed spectrum

(c) Spectrum from flow reduction of 5-nitroisophthalic acid


(a)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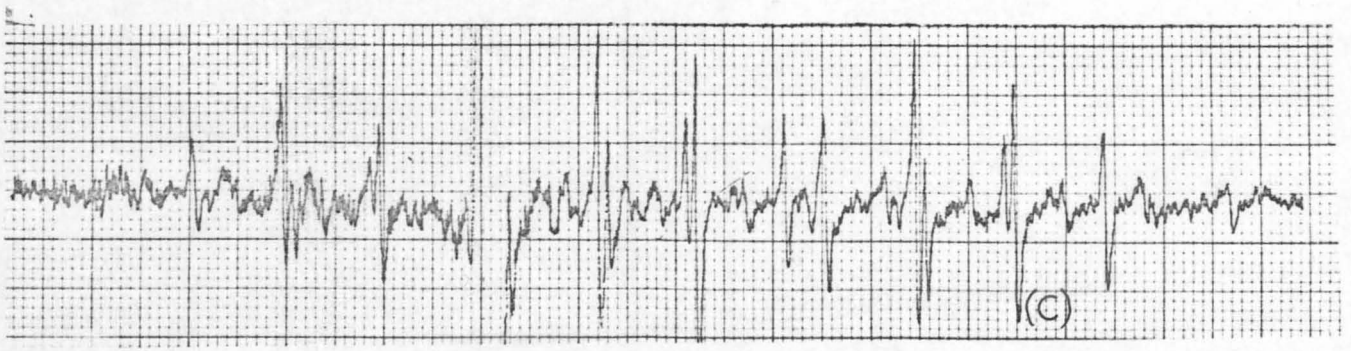
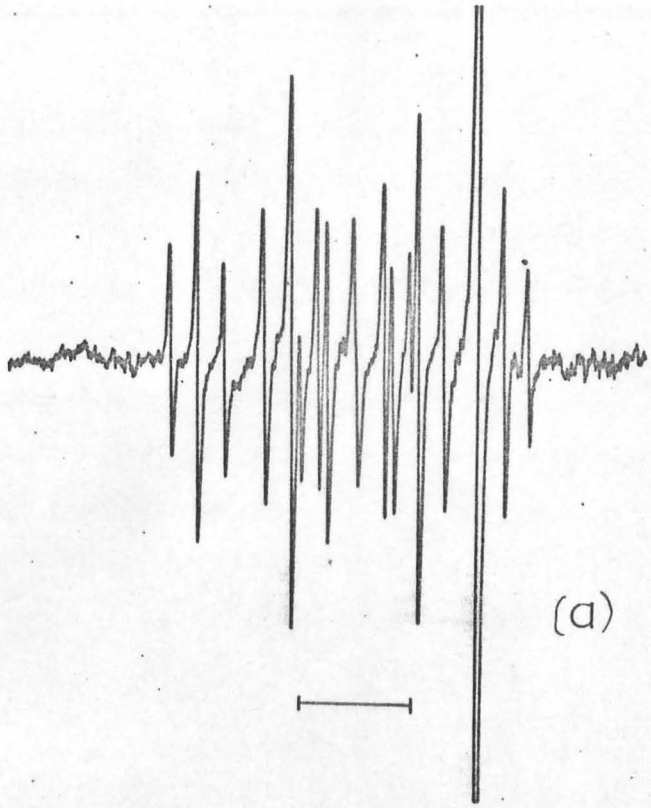

(c)

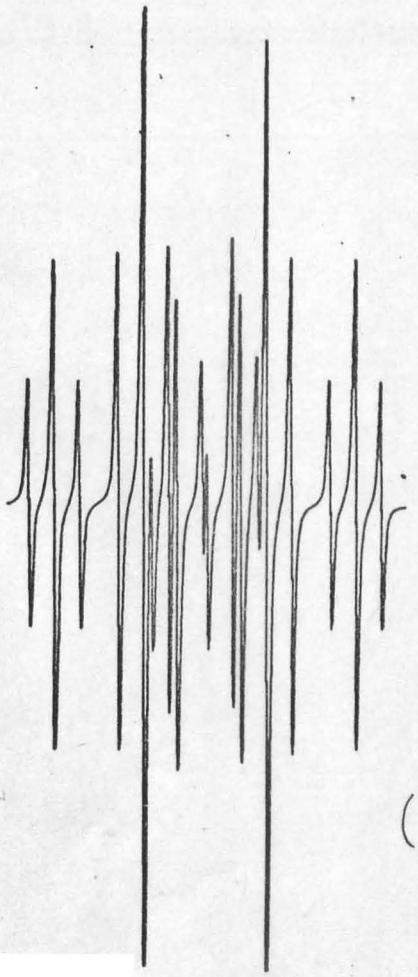
FIGURE 6.10.

(a) Spectrum from thiobenzoic acid

(b) Computer simulated spectrum



(a)



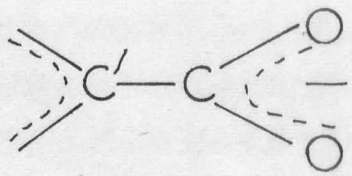
(b)

a single nitrogen atom, two almost equivalent protons and a single proton. The species remained stable for over an hour. 5-Nitroisophthalic acid gave a spectrum identical to the larger of the two species obtained in the flow reduction, this species only being detected which remained stable over an hour. Due to its low solubility, 5-nitrophthalic acid gave no detectable signal on flow reduction, but a multiline spectrum, asymmetric about the centre, was obtained on static reduction. No analysis could be made from this spectrum.

6.4. DISCUSSION

6.4.1. Theoretical Calculations

The molecular orbital calculations of pi-electron spin densities have been performed with the Hückel method and with the McLachlan procedure. For benzoic, isophthalic and terephthalic acids several resonance and Coulomb integral parameters are required, and evaluation of the empirical parameters must be carried out to give good agreement between the calculated spin densities and the experimental coupling constants. For a carboxy group there are three Coulomb integral and three resonance integral parameters. to be determined. If complete ionisation of the carboxy group is assumed, which is certain in liquid ammonia solution, then the two oxygen atoms become equivalent, as do the two carbon-oxygen bonds, thereby reducing the number of empirical parameters to be evaluated. Those now required are h_O, h_C, $k_{C'-C}$ and k_{C-O}, the labelling being



Hückel and McLachlan calculations were first made for benzoate, isophthalate and terephthalate anions using the ranges of parameters $1.0 \leq h_O \leq 2.5$, $0.1 \leq h_C \leq 0.2$, $0.8 \leq k_{C'-C} \leq 1.2$ and $0.6 \leq k_{C-O} \leq 1.6$. In all the calculations variation of h_C caused very little change in the spin density distribution and so was set to zero. The limits cover the most frequently used values.[160] The McLachlan adjustable parameter was set equal to 1.2.

Calculations were carried out, varying the parameters, until reasonable agreement with the ortho to para coupling constant ratio for the benzoate anion (experimental value 0.545) was obtained. Excellent agreement was found using the parameter values $h_O = 2.0$, $k_{C'-C} = 1.2$ and $k_{C-O} = 1.6$, with $h_C = 0$, the ratio of ortho to para McLachlan spin densities being 0.549. Such good agreement could not be found using Hückel spin densities with h- and k-values in the ranges quoted, the ratio being always too high. Comparison of the McLachlan spin densities, using these values, of the benzoate and terephthalate anions with the corresponding coupling constants, suggests an absolute value of 24.5 oe. for the McConnell Q_{CH}^{H} parameter. Agreement between coupling constants and spin densities for isophthalic acid is poor, and these values were not used in the evaluation of Q_{CH}^{H}. The Coulomb and resonance integrals are in good agreement with those of Hirayama[154] for methyl benzoate, but are higher in value than those of Nelsen[189] for phthalic anhydride. The spin densities for the anions are given in Table 6.3.

Having determined the best set of parameter values for the carboxy group, further calculations on the substituted acids can be made, particularly the methyl-substituted acids. Parameter values for the inductive, heteroatom, hyperconjugative and inductive plus hyperconjugative models were tried (see Chapter 5) and it was found that the inductive and inductive plus hyperconjugative models gave the best agreement with experiment, using the best values quoted

TABLE 6.3.

SPIN DENSITIES FOR THE RADICAL-ANIONS OF BENZOIC ACID AND DERIVATIVES[a]

Substrate	Position	Spin Densities		
		Experimental	Calculated	
			Hückel	McLachlan
Benzoic acid	1		0.169	0.167
	2, 6	0.173	0.140	0.174
	3, 5	0.033	0.026	-0.046
	4	0.318	0.232	0.317
Isophthalic acid	1, 3		0.098	0.069
	2	0.049	0.000	-0.031
	4, 6	0.280	0.269	0.378
	5	0.124	0.000	-0.101
Terephthalic acid	1, 4		0.169	0.198
	2,3,5,6	0.069	0.079	0.066
2-Methylbenzoic acid	1		0.154	0.150
	2	0.154[b]	0.110	0.126
	3	0.030	0.049	-0.011
	4	0.363	0.234	0.320
	5	0.042	0.013	-0.066
	6	0.190	0.165	0.216
3-Methylbenzoic acid	1		0.169	0.168
	2	0.180	0.160	0.204
	3	0.033[b]	0.020	-0.050
	4	0.305	0.221	0.304
	5	0.029	0.030	-0.038
	6	0.164	0.125	0.153
4-Methylbenzoic acid	1		0.156	0.150
	2, 6	0.202	0.144	0.185
	3, 5	0.047	0.016	-0.058
	4	0.328[b]	0.219	0.297

.....continued

TABLE 6.3. (continued)

Substrate	Position	Spin Densities: Experimental	Calculated: Hückel	Calculated: McLachlan
3,4-Dimethylbenzoic acid	1		0.156	0.151
	2	0.211	0.160	0.211
	3	0.035[b]	0.012	-0.060
	4	0.324[b]	0.212	0.288
	5	0.036	0.019	-0.051
	6	0.198	0.131	0.167
3,5-Dimethylbenzoic acid	1		0.170	0.170
	2, 6	0.169	0.144	0.183
	3, 5	0.029[b]	0.024	-0.042
	4	0.291	0.210	0.290
4-Methoxybenzoic acid	1		0.155	0.148
	2, 6	0.198	0.149	0.195
	3, 5	0.053	0.013	-0.063
	4		0.220	0.298
	O	0.011[c]	0.019	0.017
3-Fluorobenzoic acid	1		0.169	0.167
	2	0.189	0.146	0.185
	3	0.064[d]	0.024	-0.045
	4	0.296	0.228	0.315
	5	0.011	0.027	-0.043
	6	0.131	0.135	0.168
	F		0.002	-0.007
4-Fluorobenzoic acid	1		0.163	0.161
	2, 6	0.191	0.140	0.176
	3, 5	0.049	0.022	-0.048
	4	0.349[d]	0.226	0.304
	F		0.021	0.019

[a] "Experimental" spin densities calculated using sigma-pi parameters given in the text;

[b] Spin density obtained from methyl proton coupling constant;

[c] spin density obtained from methoxy proton coupling constant;

[d] spin density obtained from fluorine coupling constant.

in Chapter 5. Spin densities using the inductive plus hyperconjugative model, with the parameter values quoted previously, were used and the results obtained are given in Table 6.3. Correlation of the ring proton coupling constants with theoretical spin densities using the value $\left|Q_{CH}^{H}\right| = 24.5$ oe. gave good overall agreement in the methyl- and dimethyl-substituted acids, and this value was therefore used without further alteration for the remaining compounds. Again, a value of 28 oe. was used to correlate methyl proton coupling constant with the pi-electron spin density on the contiguous ring-carbon atom, a linear relation between the two being assumed.

The methoxy group in anisic acid was treated as $-\ddot{O}$, donating two electrons to the pi-system, in the calculations. The parameter values used were as given in Chapter 5, $h_O = 2.0$ and $k_{C-O} = 0.8$, no inductive effect being included, and a linear relationship between the methoxyl proton coupling constant and the spin density on the oxygen atom assumed, the constant $Q_{COCH_3}^{H}$ having the value 30 oe.

Reduction of m- and p-fluorobenzoic acids give spectra in which fluorine splitting is apparent, and calculations to find the spin density distribution are necessary to obtain assignments of coupling constants to particular ring positions. Evaluation of fluorine spin densities first requires determination of suitable Coulomb and resonance integral parameters for the fluorine atom. Two sets of parameters have been generally used in previous e.s.r. studies (see Chapter 4) and these have been used here, the two sets giving very similar results. Spin densities obtained using the parameter values $h_F = 1.6$, $k_{C-F} = 0.7$ and an auxiliary inductive parameter $h_{C-F} = 0.16$ on the carbon atom adjacent to the fluorine, are given in Table 6.3. The value $Q^F = 50$ oe. was used to correlate coupling constants with spin densities, the agreement being very good, as is apparent from Table 6.3.

Parameter values for the nitro group are required in order to

calculate pi-electron spin densities for the nitro-substituted acids. To correlate the ring proton coupling constants in these compounds with the spin densities, the nitro group parameters were found on the basis of agreement between "experimental" and calculated spin densities in p-nitrobenzoic acid. The carboxy group parameters were kept constant, while the nitro group parameters were varied until good agreement between "experimental" proton spin densities, obtained from the ring proton coupling constants using the value $\left| Q_{CH}^{H} \right| = 24.5$ oe., and calculated spin densities was obtained. No attempt was made to find the best set of parameters, as only proton assignments were required, and other parameters may equally well reproduce the experimental values. Four parameters are required for the nitro group and these generally lie within the limits[160] $0.9 \leq h_N \leq 2.4$, $1.0 \leq h_O \leq 2.0$, $0.7 \leq k_{C-N} \leq 1.2$ and $0.6 \leq k_{N-O} \leq 0.8$. Rieger and Fraenkel[163] find the values $h_N = 2.2$, $h_O = 1.4$, $k_{C-N} = 1.2$ and $k_{N-O} = 1.67$ give the best fit with experiment for nitrobenzene, but these values show poor agreement with p-nitrobenzoate ion. Keeping k_{C-N} and k_{N-O} constant, it was found that reduction of h_N and increase of h_O gave progressively better agreement, and using values of $h_N = h_O = 2.0$ reasonable agreement with experiment for p-nitrobenzoate ion was found, and these values, together with k_{C-N} and k_{N-O} as given above, were used in the calculations on nitroterephthalate and 5-nitroisophthalate. The spin densities for the three nitro acids are given in Table 6.4, together with "experimental" spin densities obtained from the non-protonated acids (see below).

6.4.2. Reduction of benzoic and substituted acids

It has been suggested from pulse radiolysis studies[177,190] that the first stage of the reduction by $e^-_{aq.}$ of benzoate and substituted benzoate ions proceeds through a rapid one-electron addition to give the corresponding

TABLE 6.4.

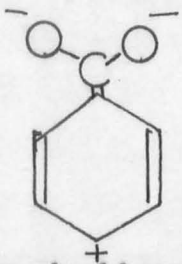
SPIN DENSITIES FOR THE RADICAL-ANIONS OF NITRO-SUBSTITUTED ACIDS[a]

Substrate	Position	Spin Densities		
		Experimental	Calculated	
			Hückel	McLachlan
4-Nitrobenzoic acid	N		0.251	0.282
	1		0.112	0.141
	2, 6	0.045	0.018	-0.022
	3, 5	0.136	0.099	0.127
	4		0.033	0.001
Nitroterephthalic acid	N		0.233	0.263
	1		0.137	0.184
	2		0.035	0.005
	3	0.154	0.056	0.060
	4		0.023	-0.009
	5	0.160	0.126	0.170
	6	0.041	0.039	-0.040
5-Nitroisophthalic acid	N		0.288	0.328
	1, 3		0.002	-0.049
	2	0.153	0.142	0.201
	4, 6	0.139	0.113	0.157
	5		0.015	-0.035

[a] The spin densities refer to the radical-anions obtained on static reduction, and "experimental" spin densities are calculated using the sigma-pi parameters given in the text. The labelling is

radical-anion. The situation is similar when reduction is carried out by metal-ammonia solutions, although such a study of benzoic acid and its ring-substituted derivatives has not been made. Due to the high reactivity of the radicals in solution, rapid and continuous renewal of the products is required to permit their observation and characterisation, and this has been accomplished by using the rapid flow technique coupled with the fast mixing device described in Chapter 3. Unambiguous assignment of the intermediates can be made due to their characteristic e.s.r. spectra.

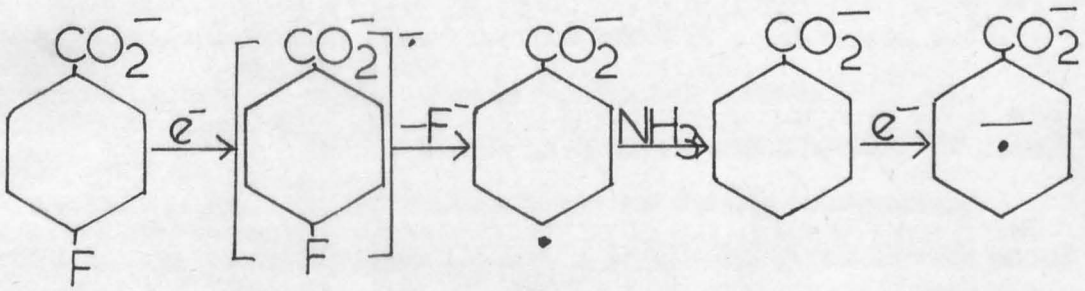
The one-electron reduction of an aromatic acid in liquid ammonia takes place much more readily than that of benzene itself. Introduction of a carboxyl group on to a benzene nucleus activates the ring towards reduction, as is shown by the ratio of the rates of reduction by $e^-_{aq.}$ of the benzoate ion and benzene itself, the factor being ca. 220. This effect can be understood in terms of the mesomeric effect of the carboxylate anion giving structures such as



Addition of a single electron should produce larger unpaired electron spin densities at the ortho- and para-positions which should be reflected in the coupling constants of the ring positions. This is indeed the case with the benzoate radical-anion, the magnitudes of the coupling constants being in the order para > ortho > meta, as is apparent from Tables 6.1 and 6.3.

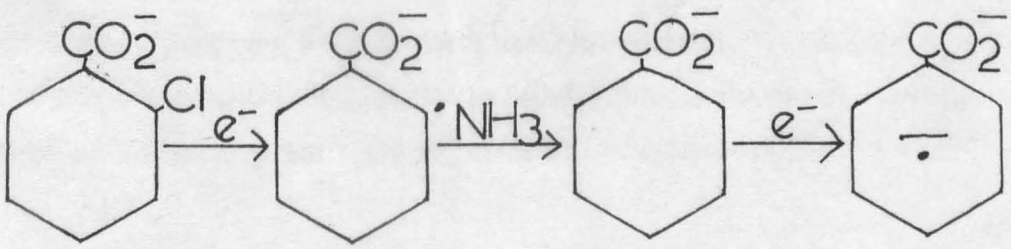
This type of mechanism is also responsible for the species obtained on reduction of isophthalic and terephthalic acids, and methyl substituted benzoic acids, e.s.r. spectra being obtained which can only arise from the one-electron reduction products of the ionised forms of these acids.

Ring substitution of benzoic acid with a halogen atom makes possible another reduction pathway; cleavage of the carbon-halogen bond may occur to give a halide ion and a free radical. This certainly seems to be the case with p-fluorobenzoic acid as is apparent from the e.s.r. spectrum obtained on its reduction. The spectrum is composed of two species, one being the benzoate radical itself and the other the fluoro-substituted species. This suggests the reaction sequence :



When the fluorine atom is in the meta-position, the carbon-fluorine bond is able to withstand the extra electron density of the radical-anion and fluorine is not lost, cf. the fluorinated benzonitriles (see Chapter 4).

As described in Section 6.3, o-chloro, m-iodo and p-bromobenzoic acids give ill-resolved spectra when a high modulation amplitude is used in their detection. These lines occur at the same field positions as do the main groups of lines of the benzoate radical and therefore could arise from reduction of the benzoate ion. If this is so, then by analogy with the reduction of the chloro- and bromo-compounds described in Chapter 4, rapid elimination of the halide ion may occur



This may also be the case with o-fluorobenzoic acid, though it is more likely that the spectrum is due to the fluoro-substituted species.

In ammonia solution, all the acids under consideration here will be completely ionised due to their low pK_a values,[191] producing a relatively high concentration of ammonium ions in the solution, according to the equation :

$$NH_3 + HA \rightleftharpoons NH_4^+ + A^-$$

where HA represents the acid. Reaction of the ammonium ions with the solvated electrons, in competition with the anions A^-, will occur, and it has been estimated[192] that the rate of the reaction between NH_4^+ and e^-_{amm} is ca. $10^{10} M^{-1} sec.^{-1}$ The rates of the reactions between the anions of the substrate acids and the ammonium ion are clearly of comparable magnitude, and if only one reduction step is required to give a species stable for a period of the order of milliseconds, then its e.s.r. spectrum will be observed. If, however, as may be the case with the chloro-, bromo- and iodo-substituted acids, the initial reaction results in the removal of halide ion, which is followed by hydrogen abstraction from the solvent and then further electron addition to give the observed radical, the reaction between NH_4^+ and e^-_{amm} will have decreased the concentration of the reductant available for reduction of the benzoate ion, and only a low concentration of the benzoate radical-dianion may be formed. This could account for the poorly resolved spectra obtained in such cases.

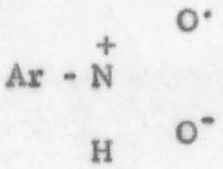
Flow reduction of p-nitrobenzoic acid gives a species whose e.s.r. spectrum indicates the presence of the corresponding radical-dianion, $ArCO_2^{2-}$, the coupling constants being in good agreement with those obtained on reduction of the acid by glucose in aqueous ethanol[113] (Table 6.2). The difference in nitrogen coupling constants is presumably due to solvation effects. No further paramagnetic products were observed.

The situation with 5-nitroisophthalic and nitroterephthalic acids is more complex. E.s.r. observations within a few msec. of mixing show, in the former case, two distinct species, one rapidly disappearing leaving only a single, relatively stable product. Reduction of nitroterephthalic acid gives initially a paramagnetic species which, over a period of one minute, is replaced by a second paramagnetic species, stable for over an hour. The transient species obtained from both acids show a doublet splitting of ca. 12 oe. extra to the expected number of coupling constants; the coupling due to nitrogen is 9.2 oe. in both cases. The two stable species show no extra doublet splitting. The magnitude of the doublet splitting is indicative of hydrogen bonded to nitrogen, as in the phenyl nitric oxide radical[193, 194] ($a_N \approx 10$ oe., $a_{NH}^{H} \approx 12$ oe.).

Reduction of nitrobenzene by metal-ammonia solutions[125] and electrolysis[65] in ammonia results in the formation of the stable nitrobenzene radical-anion. Alkali metal reduction in ammonia, followed by the addition of an alcohol or ammonium salt results in the uptake of four atomic proportions of metal per mole of substrate[195] to give phenylhydroxylamine,[196] while with excess of sodium the product is aniline.[197]

In the system under consideration here, there is little likelihood of there being a sufficient concentration of ammonium ions or reductant to permit the formation of the hydroxylamine radicals. In such a reduction, a precursor of the hydroxylamine is the corresponding nitroso compound,[198] and it has been shown that nitrosobenzene forms a stable radical-anion on electrolytic reduction in liquid ammonia,[65] therefore this should be detected in ammonia solution. Although the stable species obtained on reduction of the two nitrophthalic acids could be assigned to the corresponding nitroso radicals on spectroscopic grounds, the nitroso group is non-linear,[65, 199] and so the 4- and 6-positions of 5-nitroisophthalic acid should produce different coupling constants, but this is not found to be the case. (The

difference in coupling constants of the ortho-protons in the nitrosobenzene radical-anion is ca. 1 oe.[65,199]). Electrolytic reduction of o-nitrobenzoic acid in dimethylformamide[200] produces two radicals, an intermediate with "normal" coupling constants and a stable radical exhibiting a large splitting due to a single proton. The unstable intermediate is the o-nitrobenzoic acid radical-anion, and the stable species is formed as a further reduction product of the nitro group and contains a hydrogen bonded to the nitrogen atom;[200] this hydrogen accounts for the large splitting. In the systems under consideration in the present work, it appears that the stable radicals obtained on reduction of the two nitrophthalic acids are the radical-anions of the respective doubly-ionised acids, in contrast to the case of o-nitrobenzoic acid. One can only speculate that the unstable intermediates are due to proton-adducts with the nitro group



These give rise to the large doublet splittings observed in the transient spectra, and removal of the protons results in the stable nitro radical-anions.

APPENDICES

APPENDIX 1

The programme ESRTEST enables the computation and simulation of an experimental e.s.r. spectrum. Having been fed with the coupling constants, together with the spin and number of atoms comprising each magnetically equivalent group, calculation of line positions and relative intensities ensues, with subsequent sorting of the lines into their correct positions. A further procedure, based on a Lorentzian line-shape function enables graphical simulation of the spectrum, hence giving a direct check of the interpretation of the experimental spectrum.

The input data are as follows :

CHOICE	0 if only tabular output is required and 1 for graphical presentation.
CONFAC	Conversion factor in oersted per centimetre, which allows all measured data to be input in centimetres while output in oersteds is obtained.
CWID	Peak-to-peak line width.
HITE	Peak-to-peak height of the largest line. This factor allows scaling of the simulated spectrum to the experimental one.
N	The number of magnetically non-equivalent groups in the molecule in question.

For each group of magnetic nuclei the following data are input :

NO[M]	The number of equivalent nuclei.
SP[M]	Twice the spin for the nucleus.
CA[M]	The coupling constant for the group.

The tabulated output gives the line width and, for each group of equivalent nuclei, the number of nuclei, their spin and the coupling constant. This is followed by the position of each line, relative to the centre of the spectrum, and for each line, its degeneracy or relative intensity and the group spin quantum numbers by which its position is determined.

The programme, in Algol, is presented below.

```
ESRTEST;
"BEGIN" "INTEGER" N, XX, MOVE, CHOICE, FINAL;
"REAL" Y, YP, YY, RX, WIDTH, CWID, CONFAC, HMAX,
T, DEN, NEWPL, IGNORE, HITE;
"READ" CHOICE, CONFAC, CWID, HITE;
"IF" CHOICE=0 "THEN" "GOTO" OK;  "IF" CHOICE=1 "THEN" "GOTO" OK;
"PRINT" `YOU FORGOT THE VARIABLE THAT SELECTS WHETHER OR NOT YOU USE
THE GRAPH PLOTTER`; "GOTO" ERROR; OK:
"PRINT" ``S7`ATOM`S4`NO IN GROUP`S7`SPIN`,
SAMELINE, ``S7`SPLITTING CONSTANT`S8`LINE WIDTH`;
"PRINT" ``L1S45`CMS`S8`GAUSS`S7`CMS`S7`GAUSS`;
WIDTH:=CWID/1.27;
"PRINT" ``L2S67``, SAMELINE, ALIGNED(1,3), CWID,
``S4``, ALIGNED(1,3), CWID*CONFAC;
"READ" N;
"BEGIN" "INTEGER" "ARRAY" BLIM, NO, SP, LIMIT[1:N];
"REAL" "ARRAY" A[1:N], CA[1:N];
"INTEGER" M, L, BLIMAX, LIMAX, J, I, Z, P, K, X, CH, ML;
"REAL" CHANGE;
LIMAX:=BLIMAX:=0; ML:=1;
"PRINT" ``L2``;  "FOR" M:=1 "STEP" 1 "UNTIL" N "DO"
"BEGIN" "READ" NO[M], SP[M], CA[M];
A[M]:=CA[M]/2.54;
"PRINT" ``L1``, M, SAMELINE, ``S4``, NO[M],
``S11``, ALIGNED(1,1), SP[M]/2, ``S5``, ALIGNED(3,3), CA[M],
``S4``, ALIGNED(3,3), CA[M]*CONFAC;
BLIM[M]:=(SP[M]+1)↑NO[M];
"IF" BLIM[M]> BLIMAX "THEN" BLIMAX:= BLIM[M];
LIMIT[M]:= SP[M]* NO[M] +1;
"IF" LIMIT[M] > LIMAX "THEN" LIMAX:= LIMIT[M];
ML:=ML* LIMIT[M]; "END";
"BEGIN" "INTEGER" "ARRAY"AA[1:N,1:BLIMAX] , LL, H[1:N,1:LIMAX],
HT,QQ[0:N,1:ML];
"REAL" "ARRAY" PL[0:N,1:ML];
"INTEGER" Q, MAX, LIMIT, TEST, SCOPE, R, F, D, E, MAXI, SPIN;
"FOR" M:=1 "STEP" 1 "UNTIL" N "DO" "BEGIN" "COMMENT" WE FIND ALL POSS-
```

```
-IBLE NUCLEAR SPIN CONFIGURATIONS FOR EACH GROUP;

"INTEGER" "ARRAY"  B[0:NO[M],1:BLIM[M]];
B[0,1]:= 0;  F:= D:= E:= MAXI:=1;
NEWROW: SPIN:= -SP[M];
ADD: "IF" SPIN=SP[M]+ 2 "THEN" "BEGIN" F:=F+1;
SPIN:= -SP[M]; "END";
"IF" F> MAXI "THEN" "GOTO" NEWDEE;
B[D,E]:= B[D-1,F] + SPIN;
E:= E+1; SPIN:= SPIN + 2; "GOTO" ADD;
NEWDEE: "IF" D= NO[M] "THEN" "GOTO" CONDENSE;
MAXI:= MAXI * (SP[M] + 1); D:= D+1;  E:= F:= 1; "GOTO" NEWROW;
CONDENSE: "FOR" E:=1 "STEP"1 "UNTIL" BLIM[M] "DO"AA[M,E]:=B[NO[M],E];
J:= I:= Z:=0; NEXT: J:= J+1; NEW: Z:= Z+1;
"IF" Z> BLIM[M] "THEN" "GOTO" MORE;
I:= Z;  P:=AA[M,I];
"IF" I =1 "THEN" "GOTO" START;
"FOR" K:=1 "STEP" 1 "UNTIL" Z-1 "DO" "IF"AA[M,K]=AA[M,I] "THEN"
"GOTO" NEW;  START: LL[M,J]:= P;  H[M,J]:= 1;
"IF"  Z= BLIM[M] "THEN" "GOTO" MORE;
"FOR" I:=1+Z "STEP" 1 "UNTIL" BLIM[M] "DO"
"IF"AA[M,I] = P "THEN" H[M,J]:= H[M,J] + 1;
"GOTO" NEXT; MORE: "END";
"COMMENT"  NOW WE PUT THE GROUP QUANTUM NUMBERS TOGETHER TO GET
LINE POSITIONS AND DEGENERACIES; L:= J:= 0;  M:= Q:= MAX:= 1;
PL[0,1] := 0;  HT[0,1] := 1;
CYCLE: LIMIT:= SP[M] * NO[M] + 1; R:=0;  TEST:=0 ;
       SCOPE:=ML/ (MAX * LIMIT );
INC: "IF" J = LIMIT "THEN" "BEGIN" J:=0; Q:= Q+1;
"END";  "IF" Q > MAX "THEN" "GOTO" LEAP ;
TEST:= TEST + SCOPE;
L:=L+1; J:=J+1;
PL[M,L]:=PL[M-1,Q]+LL[M,J]*A[M];
HT[M,L]:= HT[M-1,Q] * H[M,J];
LABEL: "IF" R= TEST "THEN" "GOTO" INC;
R:= R+1; QQ[M,R]:= LL[M,J];  "GOTO" LABEL ;
LEAP: M:= M+1;  MAX:= LIMIT * MAX;  L:= J:= 0;  Q:=1;
"IF" M>N "THEN" "GOTO" FURTHER; "GOTO" CYCLE;
       "COMMENT" NOW WE SORT THE LINES BY POSITION;
FURTHER:
"FOR"X:=ML "STEP" -1 "UNTIL" 2 "DO" "FOR" J:=2 "STEP" 1 "UNTIL" X "DO"
"IF"PL[N,J-1] >PL[N,J] "THEN" "BEGIN"
CHANGE:=PL[N,J-1]; PL[N,J-1]:=PL[N,J]; PL[N,J]:= CHANGE;
CH    := HT[N,J-1];  HT[N,J-1]:= HT[N,J];  HT[N,J]:= CH    ;
"FOR"M:=1 "STEP" 1 "UNTIL" N "DO" "BEGIN"
CH    :=QQ[M,J-1]; QQ[M,J-1]:=QQ[M,J]; QQ[M,J]:= CH    ; "END"; "END";
"PRINT" ´´L4S6`LINE NO´S9`LINE POSITION´S10`DEGENERACY`,
SAMELINE, ´´S6`GROUP SPIN QUANTUM NOS`; "PRINT" ´´L1S21`CMS´S9`GAUSS`;
```

```
"PRINT" ``L2S55'';
SAMELINE; "FOR" M:=1 "STEP" 1 "UNTIL" N "DO"
"PRINT" SAMELINE, ``S1'', M;   "PRINT" ``L2'';
"FOR" J:=1 "STEP" 1 "UNTIL" ML "DO" "BEGIN"
"PRINT" ``L1S1'', J, SAMELINE, ``S7'', ALIGNED(4,3), PL[N,J]*1.27,
``S4'', ALIGNED(4,3), PL[N,J]*CONFAC*1.27, ``S3'', HT[N,J], ``S5'';
"FOR" M:=1 "STEP" 1 "UNTIL" N "DO"
"PRINT" ``S4'', ALIGNED(3,1), QQ[M,J]/2;   "END";
"IF" CHOICE=0 "THEN" "GOTO" FINIS;   PUNCH(5);
HMAX:=0;  "FOR" J:=1 "STEP" 1 "UNTIL" ML "DO" "IF" HT[N,J] > HMAX
"THEN" HMAX:=HT[N,J]; HMAX:=(HMAX*14.72)/HITE; SETORIGIN(1300,1);
MOVEPEN(-4,0);
IGNORE:=WIDTH * 1500.0; FINAL:=PL[N,ML] * 100.0 + 50.0;
"FOR" XX:=0 "STEP" 2 "UNTIL" 2*FINAL "DO" "BEGIN" RX:=XX-FINAL;
Y:=0.0;  "FOR" J:=1 "STEP" 1 "UNTIL" ML "DO" "BEGIN"
NEWPL:= PL[N,J] * 100.0;
"IF" ABS(RX-NEWPL) > IGNORE "THEN" "GOTO" CUT;
T:= (0.011547 * (RX-NEWPL)) / WIDTH;   DEN:= 1+T*T;
Y:= Y + (T * HT[N,J]) / (DEN *DEN); CUT: "END";
YP:=(1800.0*Y)/HMAX; YY:=-YP; DRAWLINE(XX,YY);
"END"; FINIS: "END"; "END"; ERROR: "END" ;
```

APPENDIX 2

The programme ESRTT2 enables the computation and simulation of any number of superimposed spectra, although for convenience it has been modified from its general form to simulate two spectra only. The method of solution is as in ESRTEST and the output is similar, the data being presented separately for each component and also for the mixed spectrum where the lines from both species are sorted by position and the graphical simulation is based upon the final line positions.

The input of data is similar to that for ESRTEST, but some additional parameters are required, the order being given below :

CHOICE	0 for tabular presentation alone and 1 for tabular presentation and graphical simulation.
MOLNO	The number of component species present ; in this work always two.
CONFAC	Conversion factor.
CENSEP	Separation of the centres of the two component spectra.

For each component the input is then :

INSTRING	The title of the species.
CWID	The peak-to-peak line width.
HITE	The peak-to-peak height of the largest line.
N	The number of magnetically non-equivalent groups.

Again, for each component the input of data for the separate groups of nuclei is :

NO The number of equivalent nuclei.

SP Twice the spin of the nucleus.

CA The coupling constant for the group.

The programme, in Algol, is presented below.

```
ESRTT2;
"BEGIN" "INTEGER" CHOICE, MOLNO, XX, MOVE, FINAL, NML, TN, C, O, J,
M, MM, CHA, NMAX, S, B, BS, GMAX, BMAX, LMAX, MLMAX;
"REAL" RX, CONFAC, CENSEP, CHAN, T, DEN, NEWPL, Y, YY, OO;
"READ" CHOICE, MOLNO, CONFAC, CENSEP;
"IF" CHOICE=0 "THEN" "GOTO" OK; "IF" CHOICE=1 "THEN" "GOTO" OK;
"PRINT" `YOU FORGOT THE VARIABLE THAT SELECTS WHETHER OR NOT
YOU USE THE GRAPH PLOTTER`; "GOTO" ERROR;
OK:
NML:=0;
"BEGIN" "INTEGER" "ARRAY" N, HMAX[1:MOLNO], HEAD[1:20];
"REAL" "ARRAY" WIDTH, CWID, GWID, HITE, IGNORE, HHMAX[1:MOLNO];
GMAX:=0;
MM:=1;
"FOR" B:=1 "STEP" 1 "UNTIL" MOLNO "DO" "BEGIN"
INSTRING(HEAD,MM);
"READ" CWID[B], HITE[B], N[B];
GWID[B]:=CWID[B]*CONFAC; WIDTH[B]:=CWID[B]/1.27;
"IF" N[B]>GMAX "THEN" GMAX:=N[B];   "END";
"BEGIN" "INTEGER" "ARRAY" BLIM, LIMIT, NO, SP[1:MOLNO,1:GMAX],
ML, BLIMAX, LIMAX[1:MOLNO];
"REAL" "ARRAY" A, GA, CA[1:MOLNO,1:GMAX];
"INTEGER" L, I, Z, P, K, X, CH;
"REAL" CHANGE;
LMAX:=BMAX:=MLMAX:=0;
"FOR" B:=1 "STEP" 1 "UNTIL" MOLNO "DO" "BEGIN"
LIMAX[B]:=BLIMAX[B]:=0;  ML[B]:=1;
"FOR" M:=1 "STEP" 1 "UNTIL" N[B] "DO"
"BEGIN" "READ" NO[B,M], SP[B,M], CA[B,M];
GA[B,M]:=CA[B,M]*CONFAC; A[B,M]:=CA[B,M]/2.54;
BLIM[B,M]:=(SP[B,M]+1)↑NO[B,M];
"IF" BLIM[B,M]>BLIMAX[B] "THEN" BLIMAX[B]:=BLIM[B,M];
"IF" BLIMAX[B]>BMAX "THEN" BMAX:=BLIMAX[B];
LIMIT[B,M]:=SP[B,M]*NO[B,M]+1;
"IF" LIMIT[B,M]>LIMAX[B] "THEN" LIMAX[B]:=LIMIT[B,M];
"IF" LIMAX[B]>LMAX "THEN" LMAX:=LIMAX[B];
ML[B]:=ML[B]*LIMIT[B,M];
"IF" ML[B]>MLMAX "THEN" MLMAX:=ML[B];
```

```
"END";   "END";
C:=ML[1];
NML:=NML+ML[1]+ML[2];
OO:=ABS(CENSEP);
"PRINT" ``L2S10 SPECTRA SEPARATION`S1'', SAMELINE, ALIGNED(1,3), OO,
``S1`CMS`S3'', ALIGNED(1,3), OO*CONFAC, ``S1`GAUSS`;
"BEGIN" "INTEGER" "ARRAY" AA[1:GMAX,1:BMAX], LL,
H[1:GMAX,1:LMAX], HT, QQ[1:MOLNO,0:GMAX,1:MLMAX], LIMIT[1:MOLNO],
DT, SS[1:NML], DQ, TQ[0:GMAX, 1:NML];
"REAL" "ARRAY" PL[1:MOLNO,0:GMAX,1:MLMAX],
DL[1:NML];
"INTEGER" Q, MAX, TEST, SCOPE, R, F, D, E, MAXI, SPIN;
"FOR" B:=1 "STEP" 1 "UNTIL" MOLNO "DO" "BEGIN"
"FOR"M:=1 "STEP" 1 "UNTIL" N[B] "DO" "BEGIN"
"COMMENT" WE FIND ALL POSSIBLE NUCLEAR SPIN CONFIGURATIONS
FOR EACH GROUP;
"INTEGER" "ARRAY" BB[0:NO[B,M], 1:BLIM[B,M]];
BB[0,1]:=0; F:=D:=E:=MAXI:=1;
NEWROW: SPIN:=-SP[B,M];
ADD: "IF" SPIN=SP[B,M]+2 "THEN" "BEGIN" F:=F+1; SPIN:=-SP[B,M]; "END";
"IF" F>MAXI "THEN" "GOTO" NEWDEE;
BB[D,E]:=BB[D-1, F]+SPIN;
E:=E+1; SPIN:=SPIN+2; "GOTO" ADD;
NEWDEE: "IF" D=NO[B,M] "THEN" "GOTO" CONDENSE;
MAXI:=MAXI*(SP[B,M]+1); D:=D+1; E:=F:=1; "GOTO" NEWROW;
CONDENSE: "FOR" E:=1 "STEP" 1 "UNTIL" BLIM[B,M] "DO"
AA[M,E]:=BB[NO[B,M], E];
J:=I:=Z:=0;
NEXT: J:=J+1;
NEW: Z:=Z+1;
"IF" Z>BLIM[B,M] "THEN" "GOTO" MORE;
I:=Z; P:=AA[M,I];
"IF" I=1 "THEN" "GOTO" START;
"FOR" K:=1 "STEP" 1 "UNTIL" Z-1 "DO"
"IF" AA[M,K]=AA[M,I] "THEN" "GOTO" NEW;
START: LL[M,J]:=P; H[M,J]:=1;
"IF" Z=BLIM[B,M] "THEN" "GOTO" MORE;
"FOR" I:=1+Z "STEP" 1 "UNTIL" BLIM[B,M] "DO"
"IF" AA[M,I]=P "THEN" H[M,J]:=H[M,J]+1;
"GOTO" NEXT; MORE: "END";
"COMMENT" NOW WE PUT THE GROUP QUANTUM NUMBERS TOGETHER
TO GET THE LINE POSITIONS AND DEGENERACIES;
L:=J:=0; M:=Q:=MAX:=1;
PL[B,0,1]:=0; HT[B,0,1]:=1;
CYCLE: LIMIT[B]:=SP[B,M]*NO[B,M]+1; R:=0; TEST:=0;
SCOPE:=0;
SCOPE:=ML[B]/(MAX*LIMIT[B]);
INC: "IF" J=LIMIT[B] "THEN" "BEGIN" J:=0; Q:=Q+1; "END";
"IF" Q>MAX "THEN" "GOTO" LEAP;
```

```
TEST:=TEST+SCOPE;
L:=L+1; J:=J+1;
PL[B,M,L]:=PL[B,M-1,Q]+LL[M,J]*A[B,M];
HT[B,M,L]:=HT[B,M-1,Q]*H[M,J];
LABEL: "IF" R=TEST "THEN" "GOTO" INC;
R:=R+1; QQ[B,M,R]:=LL[M,J]; "GOTO" LABEL;
LEAP: M:=M+1; MAX:=LIMIT[B]*MAX; L:=J:=0; Q:=1;
"IF" M>N[B] "THEN" "GOTO" FURTHER; "GOTO" CYCLE;
"COMMENT" NOW WE SORT THE LINES BY POSITION;
FURTHER: "FOR" X:=ML[B] "STEP" -1 "UNTIL" 2 "DO"
"FOR" J:=2 "STEP" 1 "UNTIL" X "DO"
"IF" PL[B,N[B], J-1]>PL[B,N[B], J] "THEN" "BEGIN"
CHANGE:=PL[B,N[B], J-1]; PL[B, N[B], J-1]:=PL[B, N[B], J];
PL[B, N[B], J]:=CHANGE;
CH:=HT[B, N[B], J-1]; HT[B, N[B], J-1]:=HT[B, N[B], J];
HT[B, N[B], J]:=CH;
"FOR" M:=1 "STEP" 1 "UNTIL" N[B] "DO" "BEGIN"
CH:=QQ[B, M, J-1]; QQ[B, M, J-1]:=QQ[B, M, J];
QQ[B,M,J]:=CH;   "END";  "END";  "END";
MM:=1;
"FOR" B:=1 "STEP" 1 "UNTIL" MOLNO "DO" "BEGIN"
"PRINT" ´´L2S20`ESR DATA FOR `;
OUTSTRING(HEAD,MM);
"PRINT" SAMELINE, B, ´´L2``;
"PRINT" ´´S7`ATOM´S4`NO IN GROUP´S7`SPIN`,
SAMELINE, ´´S7`SPLITTING CONSTANT´S8`LINE WIDTH`;
"PRINT" ´´L1S45`CMS´S8`GAUSS´S7`CMS´S7`GAUSS`;
"PRINT" ´´L2S67``, SAMELINE, ALIGNED(1,3), CWID[B],
´´S4``, ALIGNED(1,3), GWID[B], ´´L2``;
"FOR" M:=1 "STEP" 1 "UNTIL" N[B] "DO"
"PRINT" ´´L1``, M, SAMELINE, ´´S4``, NO[B,M],
´´S11``, ALIGNED(1,1), SP[B,M]/2, ´´S5``, ALIGNED(3,3), CA[B,M],
´´S4``, ALIGNED(3,3), GA[B,M];
"PRINT" ´´L4S6`LINE NO´S9`LINE POSITION´S10`DEGENERACY`,
SAMELINE, ´´S6`GROUP SPIN QUANTUM NOS`; "PRINT" ´´L1S21`CMS´S9`GAUSS`;
"PRINT" ´´L2S55``;
SAMELINE; "FOR" M:=1 "STEP" 1 "UNTIL" N[B] "DO"
"PRINT" SAMELINE, ´´S1``, M; "PRINT"´´L2``;
"FOR" J:=1 "STEP" 1 "UNTIL" ML[B] "DO" "BEGIN"
"PRINT" ´´L1S1``, J, SAMELINE, ´´S7``,
ALIGNED(4,3), PL[B, N[B], J]*1.27, ´´S4``, ALIGNED(4,3),
PL[B,N[B],J]*CONFAC*1.27, ´´S3``, HT[B,N[B],J], ´´S5``;
"FOR" M:=1 "STEP" 1 "UNTIL" N[B] "DO"
"PRINT" ´´S4``, ALIGNED(3,1), QQ[B,M,J]/2;  "END";  "END";
"COMMENT" NOW SORT OUT BOTH GROUPS OF LINES BY POSITION;
"PRINT" ´´L4S20`COMBINED DATA FOR BOTH MOLECULES´L2``;
"FOR" B:=1 "DO" "BEGIN"
J:=0:=0;
```

```
IND1: J:=J+1; O:=O+1; SS[O]:=1;
DL[O]:=PL[B,N[B],J];
DT[O]:=HT[B,N[B],J];
"FOR" M:=1 "STEP" 1 "UNTIL" N[B] "DO" DQ[M,O]:=QQ[B,M,J];
"IF" J=ML[B] "THEN" "GOTO" OUTD1;
"GOTO" IND1;  OUTD1:
"END";
"FOR" B:=2 "DO" "BEGIN"
J:=0; O:=C;
IND2: J:=J+1; O:=O+1; SS[O]:=2;
DL[O]:=PL[B,N[B],J]+(CENSEP/1.27);
DT[O]:=HT[B,N[B],J];
"FOR" M:=1 "STEP" 1 "UNTIL" N[B] "DO" DQ[M,O]:=QQ[B,M,J];
"IF" J=ML[B] "THEN" "GOTO" OUTD2;
"GOTO" IND2;  OUTD2:
"END";
"FOR" TN:=NML "STEP" -1 "UNTIL" 2 "DO"
"FOR" O:=2 "STEP" 1 "UNTIL" TN "DO"
"IF" DL[O-1]>DL[O] "THEN" "BEGIN"
CHAN:=DL[O-1]; DL[O-1]:=DL[O]; DL[O]:=CHAN;
CHA:=DT[O-1]; DT[O-1]:=DT[O]; DT[O]:=CHA;
CHA:=SS[O-1]; SS[O-1]:=SS[O];  SS[O]:=CHA;
"FOR" M:=1 "STEP" 1 "UNTIL" N[SS[O-1]] "DO" TQ[M,O]:=DQ[M,O];
"FOR" M:=1 "STEP" 1 "UNTIL" N[SS[O]] "DO" DQ[M,O]:=DQ[M,O-1];
"FOR" M:=1 "STEP" 1 "UNTIL" N[SS[O-1]] "DO" DQ[M,O-1]:=TQ[M,O];
"END";
"PRINT" ``L2S6`LINE NO`S9`LINE POSITION`S10`DEGENERACY`,
SAMELINE, ``S6`GROUP SPIN QUANTUM NOS`; "PRINT" ``L1S21`CMS`S9`GAUSS`;
"PRINT" ``L2S55``; NMAX:=0;
"FOR" B:=1 "STEP" 1 "UNTIL" MOLNO "DO"
"IF" N[B]>NMAX "THEN" NMAX:=N[B];
SAMELINE; "FOR" M :=1 "STEP" 1 "UNTIL" NMAX "DO"
"PRINT" SAMELINE, ``S1``, M; "PRINT" ``L2``;
O:=0;   SORT: O:=O+1;
"PRINT" ``L1S1``, SAMELINE, O, ``S7``;
"PRINT" SAMELINE, ALIGNED(4,3), DL[O]*1.27, ``S4``, ALIGNED(4,3),
DL[O]*CONFAC*1.27, ``S3``, DT[O], ``S5``;
"FOR" M:=1 "STEP" 1 "UNTIL" N[SS[O]] "DO" "PRINT" SAMELINE, ``S4``,
ALIGNED(3,1), DQ[M,O]/2;
"PRINT" SAMELINE, ``S5``, SS[O];
"IF" O=NML "THEN" "GOTO" OUTSORT;
"GOTO" SORT;  OUTSORT:
"IF" CHOICE=0 "THEN" "GOTO" FINIS;  PUNCH(5);
"FOR" BS:=1 "STEP" 1 "UNTIL" MOLNO "DO" HMAX[BS]:=0;
"FOR" O:=1 "STEP" 1 "UNTIL" NML "DO" "BEGIN"
BS:=SS[O];
"IF" DT[O]>HMAX[BS] "THEN" HMAX[BS]:=DT[O]; "END";
"FOR" BS:=1 "STEP" 1 "UNTIL" MOLNO "DO"
```

```
HHMAX[BS]:=(HMAX[BS]*14.72)/HITE[BS];
SETORIGIN(1300,1); MOVEPEN(-4,0);
"FOR" BS:=1 "STEP" 1 "UNTIL" MOLNO "DO"
IGNORE[BS]:=WIDTH[BS]*1500.0;
FINAL:=ENTIER(DL[NML]*100.0+200.0);
"FOR" XX:=0 "STEP" 2 "UNTIL" 2*FINAL "DO" "BEGIN"
RX:=XX-FINAL; Y:=0.0;
"FOR" O:=1 "STEP" 1 "UNTIL" NML "DO" "BEGIN"
BS:=SS[O];
NEWPL:=DL[O]*100.0;
"IF" ABS(RX-NEWPL)>IGNORE[BS] "THEN" "GOTO" CUT;
T:=(0.011547*(RX-NEWPL))/WIDTH[BS]; DEN:=1+T*T;
Y:=Y+(T*DT[O])/(DEN*DEN*HHMAX[BS]);    CUT: "END";
YY:=-(1800.0*Y);  DRAWLINE(XX,YY);
"END"; FINIS: "END";  "END";  "END";  ERROR: "END";
```

APPENDIX 3

The first programme (DIAG) used to calculate pi-electron spin densities was found to give erroneous results for the eigenvectors if degenerate eigenvalues are present. Although such degeneracy is rarely found in the compounds studied here, the results indicate a fundamental error in the matrix solution of the linear simultaneous equations, and consequently a programme library procedure was adapted to solve the secular equations. The input and output procedures were written essentially for the procedure EIGENSOLVE. The McLachlan calculation is performed after solution of the secular equations. The amount of input data is minimised by initially assigning the value zero to all Coulomb and resonance integrals, and either zero or one to all overlap integrals. The only bond and atom data then required are those values different from zero.

Input of data for the programme is as follows :

INSTRING	Title of the molecule under investigation.
LAMBDA	The adjustable McLachlan parameter λ.
ENO	The number of electrons contributing to the pi-electron framework in the neutral molecule.
ATOM NO	The number of atoms in the pi-electron framework.
BOND NO	The number of bonds in the pi-electron framework.

For each bond, the corresponding atom labels and the value of the resonance integral parameter are input. This is followed by any Coulomb integral parameter different from zero, preceded by the atom label. Finally, 0 or -1 are input : 0 if another set of data is to follow or -1

if the current set of data is the last.

All the input data is printed out, and is followed by a listing of the energy of each molecular orbital with the atom coefficients for the orbital. Finally, the Hückel and McLachlan spin densities are given for each atom position in the lowest lying antibonding molecular orbital.

```
MHSPPIN;
"BEGIN" "INTEGER" ATOM NO, BOND NO, I, J, K, P, M, MM, END, X, Y;
"REAL" LAMBDA, CHANGE;
"INTEGER" "ARRAY" HEAD[1:15];   "BOOLEAN" NEW MOLECULE;
      "PROCEDURE" SYMMETRIC QR2(N,G,X); "VALUE" N; "INTEGER" N;
      "ARRAY" G,X;
      "COMMENT" SEE ALGORITHM 254CACM;
"BEGIN" "REAL" "PROCEDURE" SUM(I,M,N,A); "VALUE" M,N;
               "INTEGER" I,M,N; "REAL" A;
               "BEGIN""REAL" S; S:=0;
                     "FOR"I:=M"STEP"1"UNTIL"N"DO" S:=S+A; SUM:=S
               "END" SUM;
      "REAL" "PROCEDURE" MAX(A,B); "VALUE" A,B; "REAL" A,B;
               MAX:="IF" A>B "THEN" A "ELSE" B;
               "PROCEDURE" HOUSEHOLDER TRIDIAGONALIZATION 2(N,G,A,B,X,
               NORM);
               "VALUE" N; "INTEGER" N; "ARRAY" G,A,B,X; "REAL" NORM;
               "COMMENT" NONLOCAL REAL PROCEDURE SUM,MAX;
               "COMMENT" SEE ALGORITHM 254 ACM;
               "BEGIN""INTEGER" I,J,K; "REAL" T,SIGMA,ALPHA,BETA,GAMMA,
               ABSB;
               "ARRAY" P[2:N]; NORM:=ABSB:=0;
               "FOR" K:=1"STEP"1"UNTIL" N-2 "DO"
               "BEGIN" A[K]:=G[K,K];
               SIGMA:=SUM(I,K+1,N,G[I,K]↑2);
               T:=ABSB+ABS(A[K]); ABSB:=SQRT(SIGMA);
               NORM:=MAX(NORM,T+ABSB); ALPHA:=G[K+1,K];
               B[K]:=BETA:= "IF" ALPHA<0 "THEN" ABSB "ELSE" -ABSB;
               "IF" SIGMA "NE" 0 "THEN"
               "BEGIN" GAMMA:=1/(SIGMA-ALPHA*BETA);
               G[K+1,K]:= ALPHA-BETA;
               "FOR" I:=K+1 "STEP" 1 "UNTIL" N"DO"
               P[I]:=GAMMA*(SUM(J,K+1,I,G[I,J]*G[J,K])
               +SUM(J,I+1,N,G[J,I]*G[J,K]));
               T:=0.5*GAMMA*SUM(I,K+1,N,G[I,K]*P[I]);
               "FOR" I:=K+1 "STEP" 1 "UNTIL" N"DO" P[I]:=P
               [I]-T*G[I,K];
```

```
                "FOR" I:=K+1 "STEP" 1 "UNTIL" N"DO"
                "FOR" J:=K+1 "STEP" 1 "UNTIL" I"DO"
                G[I,J]:=G[I,J]-G[I,K]*P[J]-P[I]*G[J,K];
                "FOR" I:=2   "STEP" 1 "UNTIL" N"DO"
                P[I]:=GAMMA*SUM(J,K+1,N,X[I,J]*G[J,K]);
                "FOR"I:=2"STEP"1"UNTIL" N"DO"
                "FOR"J:=K+1"STEP"1"UNTIL" N"DO"
                X[I,J]:=X[I,J]-P[I]*G[J,K]
                "END"
                "END" K;
                A[N-1]:=G[N-1,N-1]; A[N]:=G[N,N]; B[N-1]:=G[N,N-1];
               T:=ABS(B[N-1]);
                NORM:=MAX(NORM,ABSB+ABS(A[N-1])+T);
                NORM:=MAX(NORM,T+ABS(A[N]))
        "END" HOUSEHOLDER TRIDIAGONALIZATION 2;
"INTEGER" I,J,K,M,M1; "REAL" T,NORM,EPS,SINE,COSINE,LAMBDA,
                MU,A0,A1,B0,BETA,X0,X1;
        "ARRAY" A[1:N],B[0:N],C[0:N-1],CS,SN[1:N-1];
        "FOR"I:=1"STEP"1"UNTIL" N"DO"
        "BEGIN""COMMENT" SET X EQUAL TO THE IDENTITY MATRIX;
                X[I,I]:=1;
                "FOR"J:=I+1 "STEP"1"UNTIL"N "DO" X[I,J]:=X[J,I]:=0
        "END"I;
        HOUSEHOLDER TRIDIAGONALIZATION 2(N,G,A,B,X,NORM);
        EPS:=NORM*3.6410-12;
        "COMMENT" SEE ALGORITHM 254 CACM;
        B[0]:=MU:=0; M:=N;
        INSPECT: "IF" M=0 "THEN""GOTO" RETURN "ELSE" I:=K:=M1:=M-1;
         "IF" ABS(B[K]) "LE" EPS "THEN"
        "BEGIN" G[M,M]:=A[M]; M:=K; "GOTO" INSPECT "END";
        "FOR" I:=I-1 "WHILE" ABS(B[I])>EPS "DO" K:=I;
        "COMMENT" FIND EIGENVALUES OF LOWER 2*2;
         B0:=B[M1]↑2; A1:=SQRT((A[M1]-A[M])↑2+4*B0);
        T:=A[M1]*A[M]-B0; A0:=A[M1]+A[M];
        LAMBDA:=0.5*("IF" A0"GE"0"THEN"A0+A1 "ELSE" A0-A1);
        T:=T/LAMBDA; "COMMENT" COMPUTE THE SHIFT;
        "IF" ABS (T-MU)<0.5*ABS(T) "THEN" MU:=LAMBDA:=T
        "ELSE""IF" ABS(LAMBDA-MU)<0.5*ABS(LAMBDA) "THEN" MU:=LAMBDA
        "ELSE""BEGIN" MU:=T; LAMBDA:=0 "END";
        A[K]:=A[K]-LAMBDA; BETA:=B[K];
        "FOR" J:=K"STEP"1"UNTIL" M1 "DO"
        "BEGIN""COMMENT" TRANSFORMATION ON THE LEFT;
         A0:=A[J]; A1:=A[J+1]-LAMBDA; B0:=B[J];
         T:=SQRT(A0↑2+BETA↑2);
         COSINE:=CS[J]:=A0/T; SINE:=SN[J]:=BETA/T;
         A[J]:=COSINE*A0+SINE*BETA; A[J+1]:=-SINE*B0+COSINE*A1;
         B[J]:=COSINE*B0+SINE*A1; BETA:=B[J+1];
         B[J+1]:=COSINE*BETA; C[J]:=SINE*BETA
        "END"J;
```

```
      B[K-1]:=C[K-1]:=0;
      "FOR"J:=K"STEP"1"UNTIL" M1 "DO"
      "BEGIN""COMMENT" TRANSFORMATION ON THE RIGHT;
       SINE:=SN[J]; COSINE:=CS[J];
       A0:=A[J]; B0:=B[J];
       B[J-1]:=B[J-1]*COSINE+C[J-1]*SINE;
       A[J]:=A0*COSINE+B0*SINE+LAMBDA;
       B[J]:=-A0*SINE+B0*COSINE; A[J+1]:=A[J+1]*COSINE;
             "FOR" I:=1   "STEP" 1 "UNTIL" N"DO"
       "BEGIN" X0:=X[I,J]; X1:=X[I,J+1];
       X[I,J]:=X0*COSINE+X1*SINE; X[I,J+1]:=-X0*SINE+
      X1*COSINE
       "END" I
       "END" J;
       A[M]:=A[M]+LAMBDA; "GOTO" INSPECT;
       RETURN: "END" SYMMETRIC QR 2;
       "PROCEDURE" EIGENSOLVE(A,B,X,N,NONDEF); "VALUE" N; "INTEGER" N;
"LABEL" NONDEF;"ARRAY"A,B,X; "COMMENT"ALG297 VOL10 NO3 MAR67;
       "BEGIN""INTEGER" I,J,K,JLESS1,ILESS1,ADI,BDI;
       "REAL" T,SUM,XIJ,LENGTH; "BOOLEAN"RECIP;
       "PROCEDURE" LCHOLESKI(A,N,FAIL); "VALUE" N; "INTEGER" N;
       "LABEL"FAIL;"ARRAY"A;"COMMENT"SEE ALGORITHM297;
       "BEGIN""INTEGER" I,J,K,JLESS1; "REAL" AJJ,AJK,AIJ;
       JLESS1:=0; "FOR" J:=1"STEP"1"UNTIL"N"DO"
       "BEGIN"AJJ:=A[J,J];
       "FOR"K:=1"STEP"1"UNTIL"JLESS1 "DO"
       "BEGIN"AJK:=A[J,K]; AJJ:=AJJ-AJK*AJK
       "END";
       "IF" AJJ"LE"0.0"THEN""GOTO"FAIL;
       AJJ:=A[J,J]:=SQRT(AJJ);
       "FOR"I:=J+1"STEP"1"UNTIL"N"DO"
       "BEGIN" AIJ:=A[I,J]; "FOR"K:=1"STEP"1"UNTIL"JLESS1
       "DO"AIJ:=AIJ-A[I,K]*A[J,K];
       A[I,J]:=AIJ/AJJ
       "END";
       JLESS1:=J
       "END" J;
       "END" LCHOLESKI;
       "COMMENT" SEE ALG 297 VOL10 NO3 MAR67  ;
       ADI:=SIGN(A[1,1]); X[1,1]:=T:=B[1,1]; BDI:=SIGN(T);
             "FOR" I:=2   "STEP" 1 "UNTIL" N"DO"
       "BEGIN"T:=A[I,I]; "IF" T=0.0 "OR"(T>0 "EQUIV" ADI<0)
            "THEN" ADI:=0;
      X[I,I]:=T:=B[I,I]; "IF" T=0.0 "OR"(T>0 "EQUIV" BDI<0)
            "THEN" BDI:=0
       "END";
       RECIP:="FALSE"; "COMMENT" PREPARE TO SOLVE (A-LAMBDA B) X=0;
       "IF" BDI=0 "THEN""GOTO" SWAP; "COMMENT" B IS NONDEFINITE;
       "IF"BDI<0 "THEN"
```

```
"BEGIN""COMMENT" PREPARE TO SOLVE (A-(-LAMBDA)(-B))X=0;
        "FOR" I:=1   "STEP" 1 "UNTIL" N"DO"
        "FOR" J:=1   "STEP" 1 "UNTIL" I"DO"B[I,J]:=-B[I,J]
"END";          NEWTRY: LCHOLESKI(B,N,SWAP); "GOTO" OK;
SWAP: "IF" RECIP "THEN" "GOTO" NONDEF; RECIP:= "TRUE";
"COMMENT" PREPARE TO SOLVE (B-(1/LAMBDA)A)X=0;
"IF" ADI=0 "THEN""GOTO" SWAP; "COMMENT" TO ESCAPE,
SINCE A IS ALSO NONDEFINITE; "IF" ADI<0 "THEN"
"BEGIN""COMMENT" PREPARE TO SOLVE (B-(-1/LAMBDA)(-A))X=0;
        "FOR" I:=1   "STEP" 1 "UNTIL" N"DO"
"BEGIN"B[I,I]:=A[I,I]; A[I,I]:=X[I,I];
        "FOR"J:=I+1"STEP"1"UNTIL" N"DO"
"BEGIN" B[J,I]:=-A[I,J]; A[J,I]:=B[I,J]
 "END";
"END";
"END"
"ELSE""BEGIN""COMMENT" PREPATE TO SOLVE (B-(1/LAMBDA)A)X=0;
        "FOR" I:=1   "STEP" 1 "UNTIL" N"DO"
 "BEGIN" B[I,I]:=A[I,I]; A[I,I]:=X[I,I];
        "FOR"J:=I+1"STEP"1"UNTIL" N"DO"
 "BEGIN"B[J,I]:=A[I,J]; A[J,I]:=B[I,J]
      "END";
  "END";
"END";
 "GOTO" NEWENTRY;
 "COMMENT" FORM C=(L)†-1 A(L´)†-1 BY LX=A,CL´=X,CREPLACES A;
OK: JLESS1:=0; "FOR" J:=1"STEP"1"UNTIL" N "DO"
 "BEGIN" ILESS1:=0; "FOR" I:=1"STEP" 1 "UNTIL" J "DO"
 "BEGIN" SUM:=A[J,I]; "FOR" K:=1"STEP" 1 "UNTIL" ILESS1 "DO"
 SUM:=SUM-X[K,J]*B[I,K]; SUM:=X[I,J]:=SUM/B[I,I];
 "FOR" K:=1"STEP" 1 "UNTIL" JLESS1 "DO"
 SUM:=SUM-( "IF" K "LE" I "THEN" A[I,K] "ELSE"
 A[K,I])*B[J,K]; A[J,I]:=SUM/B[J,J]; ILESS1:=I
 "END";
 JLESS1:=J
 "END";
 "COMMENT" GLOBAL CALL OF SYMMETRIC QR2 TO SOLVE.....;
SYMMETRIC QR2(N,A,X);
 "COMMENT" CHANGE THE Y VECTORS, NOW IN X BY L´X=Y AND
 NORMALIZE TO UNIT LENGTH; "FOR" J:=1"STEP"1"UNTIL" N "DO"
 "BEGIN" LENGTH:=0.0; "FOR" I:=N"STEP"-1"UNTIL"1 "DO"
 "BEGIN" SUM:=X[I,J]; "FOR" K:=I+1 "STEP" 1 "UNTIL" N "DO"
 SUM:=SUM-B[K,I]*X[K,J]; XIJ:=X[I,J]:=SUM/B[I,I];
 LENGTH:=LENGTH+XIJ*XIJ
 "END";
 LENGTH:=SQRT(LENGTH);
 "FOR"I:=1"STEP"1"UNTIL"N"DO" X[I,J]:=X[I,J]/LENGTH
 "END";
```

```
        "COMMENT" TAKE THE RECIPROCALS AND/OR CHANGE THE SIGNS OF THE
        ROOTS IF NECESSARY; "FOR"I:=1"STEP"1"UNTIL" N"DO"
        "IF" RECIP "THEN"
        "BEGIN""IF" ADI<0 "THEN" A[I,I]:=-1.0/A[I,I]
        "ELSE"A[I,I]:=1.0/A[I,I]
        "END" "ELSE" "IF" BDI<0 "THEN" A[I,I]:=-A[I,I]
        "END" EIGENSOLVE;
START:
"PRINT" ´´L2S10`HUCKEL AND MCLACHLAN SPIN DENSITIES FOR `;
MM:=1;
INSTRING(HEAD,MM);
MM:=1;
OUTSTRING(HEAD,MM);
"READ" LAMBDA, ENO, ATOM NO, BOND NO;
"PRINT" ´´L6S26`NO OF ELECTRONS`, SAMELINE, ENO;
"PRINT" ´´L2S30`NO OF ATOMS`, SAMELINE, ATOM NO;
"PRINT" ´´L2S30`NO OF BONDS`, SAMELINE, BOND NO;
"PRINT" ´´L2S30`LAMBDA`, SAMELINE, ´´S11``, LAMBDA;
"BEGIN" "REAL" "ARRAY" H, S, CC, COEFF[1:ATOM NO,1:ATOM NO],
ENERGY[1:ATOM NO];
"PROCEDURE"PRINT ENERGY AND COEFF(A,W,N);
"VALUE"N;"INTEGER"N;"ARRAY"A,W;
"BEGIN""COMMENT" PRINTS ENERGIES AND COEFFICIENTS IN 10 COLUMNS WITH
HEADINGS;
"INTEGER"I,J,T,Q;
"FOR"Q:=1"STEP"10"UNTIL"N"DO"
"BEGIN"T:="IF"N-Q<10"THEN"N"ELSE"Q+9;
      "PRINT"´´L5S30`ENERGIES IN ASCENDING ORDER´L2``;
      "FOR"I:=Q"STEP"1"UNTIL"T"DO""PRINT"PREFIX(´´S2``),W[I];
      "PRINT"´´L3S32`COEFFICIENTS IN COLUMNS´L2``;
      "FOR"I:=1"STEP"1"UNTIL"N"DO"
      "BEGIN""FOR"J:=Q"STEP"1"UNTIL"T"DO""PRINT"PREFIX(´´S2``),A[J,I];
      "PRINT"´´L``;
      "END"
"END"
"END"OF PRINT ENERGY AND COEFF;
"PROCEDURE" MCLACHLAN(AN, H, L, C, E);
"VALUE" AN, H, L;   "INTEGER" AN, H;   "REAL" L;   "ARRAY" C, E;
"COMMENT" CALCULATES AND PRINTS HUCKEL AND MCLACHLAN SPIN
DENSITIES FOR ANION RADICALS WITH ANY NUMBER OF DEGENERATE
LOWEST ANTIBONDING ORBITALS;
"BEGIN" "INTEGER" X, Y, I, J, S, T;
"REAL" D;
"REAL" "ARRAY" SUMPI, SPI, PI[1:AN,1:AN], SD, SUMRHO, RHO[1:AN];
"FOR" X:=1 "STEP" 1 "UNTIL" AN "DO"
"FOR" Y:=1 "STEP" 1 "UNTIL" AN "DO" "BEGIN"
SPI[X,Y]:=0.0;
"FOR" J:=H+1 "STEP" 1 "UNTIL" AN "DO" "BEGIN"
```

```
SUMPI[X,Y]:=0.0;
"FOR" I:=1 "STEP" 1 "UNTIL" H "DO"
SUMPI[X,Y]:=SUMPI[X,Y]+((C[I,X]*C[I,Y])/(E[J]-E[I]));
SPI[X,Y]:=SPI[X,Y]+SUMPI[X,Y]*(C[J,X]*C[J,Y]);   "END";
PI[X,Y]:=-(4*SPI[X,Y]);   "END";
"FOR" X:=1 "STEP" 1 "UNTIL" AN "DO" "BEGIN"
S:=1;   T:=H+1;
D:=C[T,X]↑2;
SDIN:   T:=T+1;
"IF" ABS(E[T]-E[T-1])<10-3 "THEN" "GOTO" DENIN "ELSE" "GOTO" SPIND;
DENIN:   D:=D+C[T,X]↑2;   S:=S+1;   "GOTO" SDIN;
SPIND:   D:=D/S;   SD[X]:=D;   "END";
"FOR" X:=1 "STEP" 1 "UNTIL" AN "DO" "BEGIN"
SUMRHO[X]:=0.0;
"FOR" Y:=1 "STEP" 1 "UNTIL" AN "DO"
SUMRHO[X]:=SUMRHO[X]+(PI[X,Y]*SD[Y]);
RHO[X]:=SD[X]-(L*SUMRHO[X]);   "END";
"PRINT" ``L2S20`ATOM`S14`SPIN DENSITIES`L1``;
"PRINT" ``S35`HUCKEL`S9`MCLACHLAN`L2``;
"FOR" X:=1 "STEP" 1 "UNTIL" AN "DO"
"PRINT" ``S14``, SAMELINE, X, ``S6``, PREFIX(``S2``), SD[X],
``S6``, PREFIX(``S2``), RHO[X], ``L1``;
"END" OF MCLACHLAN;
"COMMENT" NOW ASSIGN S-MATRIX ELEMENTS NEGLECTING OVERLAP, AND
INITIALLY SET ALL ELEMENTS OF H-MATRIX TO ZERO, THEN READ IN ANY
RELEVANT BOND AND ATOM DATA;
"FOR" I:=1 "STEP" 1 "UNTIL" ATOM NO "DO"
"FOR" J:=1 "STEP" 1 "UNTIL" ATOM NO "DO" "BEGIN"
"IF" J=I "THEN" S[I,J]:=1.0 "ELSE" S[I,J]:=0.0;
H[I,J]:=0.0;   "END";
"COMMENT" INPUT OF BOND DATA;
"PRINT" ``L2S13`BOND`S10`K-VALUES`;
"FOR" I:=1 "STEP" 1 "UNTIL" BOND NO "DO" "BEGIN"
"READ" K, P;   "READ" H[K,P];
H[P,K]:=H[K,P];
"PRINT" ``L1``, SAMELINE, PREFIX(``S2``), K, P, PREFIX(``S4``),
H[K,P];   "END";
"COMMENT" INPUT OF ATOM DATA;
"PRINT" ``L2S13`ATOM`S10`H-VALUES`;
NEW:   "READ" K;
"IF" K "LE" 0 "THEN" "GOTO" END DATA;
"READ" P;
"IF" P "NE" K "THEN" "GOTO" FAIL;
"READ" H[K,K];
"PRINT" ``L1``, SAMELINE, PREFIX(``S2``), K, P, PREFIX(``S4``),
H[K,K];
"GOTO" NEW;
END DATA:   NEW MOLECULE:=K=0;
```

```
"COMMENT" NEW MOLECULE IF TRUE MEANS A NEW SET OF DATA FOLLOWS
THIS SET, IF FALSE THAT THIS IS THE LAST SET OF DATA FOR THIS RUN;
M:=ENO "DIV" 2;
"COMMENT" M GIVES THE NUMBER OF DOUBLY OCCUPIED ORBITALS;
EIGENSOLVE(H, S, COEFF, ATOM NO, FAILED);
"GOTO" MHTN;
FAILED:   "PRINT" ``L2S10`AND YET THEIR REWARD APPEARETH NOT,`;
"PRINT" ``L2S10`AND THEIR LABOUR HATH NO FRUITE....`;
"GOTO" FINISH;
MHTN:
"FOR" I:=1 "STEP" 1 "UNTIL" ATOM NO "DO" ENERGY[I]:=H[I,I];
"COMMENT" NOW SORT OUT THE EIGENVALUES IN DECREASING ORDER,
IE. INCREASING ENERGY, AND CORRESPONDINGLY CHANGE THE
EIGENVECTORS;
"FOR" X:=ATOM NO "STEP" -1 "UNTIL" 2 "DO"
"FOR" I:=2 "STEP" 1 "UNTIL" X "DO"
"IF" ENERGY[I-1]<ENERGY[I] "THEN" "BEGIN"
CHANGE:=ENERGY[I-1];   ENERGY[I-1]:=ENERGY[I];   ENERGY[I]:=CHANGE;
"FOR" J:=1 "STEP" 1 "UNTIL" ATOM NO "DO" "BEGIN"
CHANGE:=COEFF[J,I-1];   COEFF[J,I-1]:=COEFF[J,I];
COEFF[J,I]:=CHANGE;   "END";   "END";
"COMMENT" NOW EFFECTIVELY TRANSPOSE THE COEFF MATRIX SO THE
PRINT ENERGY AND MCLACHLAN PROCEDURES WORK;
"FOR" I:=1 "STEP" 1 "UNTIL" ATOM NO "DO"
"FOR" J:=1 "STEP" 1 "UNTIL" ATOM NO "DO"
CC[I,J]:=COEFF[I,J];
"FOR" I:=1 "STEP" 1 "UNTIL" ATOM NO "DO"
"FOR" J:=1 "STEP" 1 "UNTIL" ATOM NO "DO"
COEFF[I,J]:=CC[J,I];
PRINT ENERGY AND COEFF(COEFF, ENERGY, ATOM NO);
"COMMENT" NOW CALCULATE AND PRINT SPIN DENSITIES;
MCLACHLAN(ATOM NO, M, LAMBDA, COEFF, ENERGY);
"END";
"IF" NEW MOLECULE "THEN" "BEGIN"
"PRINT" ``F``;   "GOTO" START;   "END" "ELSE"
"GOTO" FINISH;
FAIL:   "PRINT" `FAILURE IN ATOM DATA`;
FINISH:   "END" OF MHSPIN;
```

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